NOTE

This Microfiche meets the quality requirements of the American National Standard for Microfiche of Documents (ANSI PH5.9-1975). However, because of imperfections in the document from which it was made, it contains images that are illegible or difficult to read. The source document for this microfiche is the best copy that could be obtained prior to filming.

CIS Congressional Information Service, Inc.
Washington, D.C.

Potential of Ceramic Materials to Replace Cobalt, Chromium, Manganese, and Platinum in Critical Applications

by

Elaine P. Rothman
George B. Kenney
H. Kent Bowen

Materials Processing Center
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Submitted to:

Office of Technology Assessment
Congress of the United States
Washington, D.C. 20510

Final Report:
Contract Number 333-6530.2
January 6, 1984

"These Working Papers were prepared by outside contractors as an input to an ongoing OTA Assessment. They do not necessarily reflect the analytical findings of OTA. These Working Papers have been neither reviewed nor approved by the Technology Assessment Board."

J952-57

Potential of Ceramic Materials to Replace Cobalt, Chromium, Manganese, and Platinum in Critical Applications

"This is an OTA Working Paper that was used in preparing OTA's final Assessment Report on Strategic Materials: Technologies to Reduce U.S. Import Vulnerability. OTA makes these Working Papers available for the use of readers desiring a more detailed or technical discussion of an issue than can normally be accommodated in our final Report. As an OTA Working Paper, this report has not been reviewed or approved by the Technology Assessment Board. The findings and conclusions expressed in the report are those of the authors and do not necessarily reflect the views of OTA, the Strategic Materials Advisory Panel, or the Technology Assessment Board."

Table of Contents

List of Tables		ii
List of Figures		v
1.	Executive Summary	1
2.	Definition of Ceramics	13
3.	Cobalt	53
4.	Chromium and Manganese	67
5.	Platinum	79
6.	Heat Engines	89
7.	Cutting Tools	151
8.	Heat Exchangers	172
9.	Wear-Resistant Applications	188
10.	Nondestructive Evaluation of Ceramics	200
11.	Institutional Barriers to Expanded Advanced Ceramics Usage	211
12.	Prospects for Advanced Ceramics	226
Appendix - Materials Supply		259

List of Tables

Chapter 1

1.1 Advanced Ceramics Supporting High Tech Industries for 1990's
1.2 Potential of Advanced Ceramics to Substitute for Strategic Materials in Critical Applications

Chapter 2

2.1 U.S. Ceramic Market Data
2.2 Industrial Functions of Fine Ceramics
2.3 High Technology Ceramics Markets (1980 - $M)
2.4 Classification of High Tech Ceramics by Function with Possible Areas of Substitution for Strategic Metals
2.5 Production Techniques for Fine Ceramics
2.6 Traditional Ceramic Materials and Their Uses
2.7 Properties of Aluminas Used in Fine Ceramics
2.8a Strength and Toughness of Glass-Fiber Composites
2.8b Strength and Toughness of Glass-Fiber Composites Made by Co-pyrolysis
2.9 Structural Applications for High Technology Ceramics
2.10 Properties of Ceramics and Metals

Chapter 3

3.1 Cobalt use in the United States, %
3.2 U.S. Consumption of Cobalt, by End Use
3.3 Typical Applications of Cobalt-Bonded Cemented Carbides
3.4 Cobalt-Free Permanent Magnet Materials
3.5 Cobalt-Containing Permanent Magnet Materials

Chapter 4

4.1 Projections and Forecasts for U.S. Chromium Demand, by End Use
4.2 U.S. Consumption of Chromium Ferroalloys and Metal in 1981, by End Use
4.3 Chromium Usage in U.S.-Built Passenger Cars Powered by Conventional Otto Cycle Piston Engines
4.4 Alternative for Ceramic Products

Chapter 5

5.1 Platinum Group Metals Sold to Consuming Industries in the United States

Chapter 6

6.1 Meradcom-Solar 10KW Program Highlights
6.2 Summary of High Technology Ceramic Components for Adiabatic Engines in Japan and U.S.

Chapter 6 cont'd

6.3 Typical Desired Materials Properties for an Adiabatic Type Diesel Engine
6.4 Mechanical property Comparison Polycrystalline PSZ
6.5 Ceramic Market Potential for Heat Engines
6.6 The Market Potential for Turbochargers
6.7 Projection of Chromium and Cobalt Use in Gas Turbines
6.8 Representative Engine Design Repirements for Ceramics Applications
6.9 Comparison of Automotive Gas Turbine Engines
6.10 Typical Properties of Silicon Carbide and Silicon Nitride Ceramics
6.11 A Comparison of Major Characteristics of Dense Forms of Silicon Carbide and Silicon Nitride
6.12 Differences in the Properties of High Performance Ceramics Produced by Slip-casting, Hot Pressing, and Reaction Bonding
6.13 Airecraft Gas Turbine Engines: Estimated Worth and Development Costs in 1977 Dollars
6.14 Features of Gas Turbine Engines by Application
6.15 Summary of Market Potential for Selected Ceramic Parts
6.16 The Market for Ceramic Parts in Stationary Gas Turbine Electric Generators
6.17 Ceramic Vane Estimated Production Costs
6.18 Cost Summary for Fabricating Ceramic Vane Nozzle

Chapter 7

7.1 Comparison of Physical Properties of Sintered Alumina and Cemented Carbide
7.2 Main Characteristics of Several Types of Cutting Tool Materials
7.3 Comparison of Tool Materials
7.4 Field Test Results on Rough Machining of Blade Drum
7.5 Trade Data, Metal Cutting Tools
7.6 Ceramic Cutting Tool Materials and Uses

Chapter 8

8.1 Oxidation and Sulfidation Resistant Alloy Selection
8.2 Properties and Prices of Selected Ceramic Materials
8.3 System Fabrication and Installation Expense

Chapter 9

9.1 Ceramics and Their Competitors: Application Comparisons

Chapter 10

10.1 Comparison of Several NDE Techniques for Flaw Detection in Silicon Carbide Heat-Exchanger Tubing
10.2 Estimated Sensitivity of NDE Methods for Flaw Detection in Silicon Carbide Heat-Exchanger Tubing

Chapter 11

11.1 Properties of Ceramics and Metals
11.2 Mechanical Property Comparison - Polycrystalline PSZ
11.3 Strength as a Function of Surface Finish on Sintox FA 95% Alumina Die Pressed Tile Material
11.4 Strength as a Function of Forming Route on Sintox FA 95% Alumina Material
11.5 Resistance of Ceramics to Chemical Attack - Crucible Tests

Chapter 12

12.1 Physical Properties of Ceramic Materials
12.2 High Technology Ceramics Markets (1980 - $M)
12.3 Typical Manufacturing Cost for High Value Added Ceramics
12.4 R&D of Fine Ceramics by Government-Affiliated Laboratories and Institutes
12.5 Structural Ceramic Market Penetration

Appendix

AP.1 Ceramic Mineral Source
AP.2 SiC Consumption by End Use, 1981
AP.3 Prices of Silicon Carbide: 1970 to 1980
AP.4 Domestic Alumina consumption in the Ceramic Industry by End Use, 1981
AP.5 Domestic Zirconia Consumption by End Use, 1981
AP.6 Mechanical Property Comparison Polycrystalline PSZ

List of Figures

Chapter 2

2.1 Simplified Flow Diagram of Slip Casting Art Ware
2.2 Simplified Flow Diagram of an Extrusion Process
2.3 Simplified Flow Diagram of an Operating Dry Press Operation
2.4 Schematic Drawing of Injection End of Two-Stage Screw Plunger Machine
2.5 Schematic of Processing Fiber Composites

Chapter 3

3.1 Classification of Magnetic Materials

Chapter 5

5.1 Uses of Platinum and Palladium in 1981

Chapter 6

6.1 General History of Ceramic Programs for Engines
6.2 Predicted Production Date Adiabatic Engine Spin-Offs ENgine Program
6.3 Energy Balance Comparison (Diesel Engine)
6.4 Cross-Section End-View of 750 Hp Diesel Engine
6.5 Thermal Expansion of Typical Ceramics and Cast Iron
6.6 Thermal Conductivities of Typical Ceramics
6.7 Cummins NH Turbocompound Diesel Engine
6.8 Basic Design of Ceramic Rotor and Metallic Shaft
6.9 Strength of Silicon Nitride Materials vs. Required Strengths for Engine Components
6.10 Strength of Silicon Nitride Materials vs. Required Strengths for Engine Components
6.11 Incorporation of Ceramics into the Basic Design of the Gas Turbine Engine
6.12 Turbine Blade Cost Comparisons: Aircooled Metal vs. Uncooled Ceramic
6.13 Redesign of Ceramic Parts to Reduce Stress Concentrations

Chapter 7

7.1 Change in Productivity via the Introduction of New Cutting Tool Materials
7.2 Performance of Selected Ceramic Cutting Tools in Gray Cast Iron Machining Compared to TiC Coated WC-Co Tool

Chapter 8

8.1 Three Types of Gas Flow Paths Used in Recuperators
8.2 Axial Counterflow Heat Exchanger Concept
8.3 Indirect Exhuast Coal-Fired Combined Cycle

Chapter 9

9.1 Properties of Silicon Carbide (Hexology™) and the Materials for Which it Can Substitute in Seal Applications
9.2 Wear Versus Hardness for Several Classes of Material

Chapter 12

12.1 Typical Ceramic Green Microstructure
12.2 Manufacturing Forces Smaller than Interparticle Forces
12.3 Effect of Greenware Structural Flaws
12.4 Submicron, Monosized Ceramic Powders
12.5 Fabrication with Ideal, Close-Packed Powders
12.6 Function and Use of Fine Ceramics (Examples)
12.7 Performance Parameters of Ceramics as Mechanical Materials
12.8 A comparison of SiC Production Costs
12.9 A Generalized Comparison of Structural Ceramics Activity
12.10 U.S. Funding of Ceramic Gas Turbine Engine Development Yrs. 1974-1981

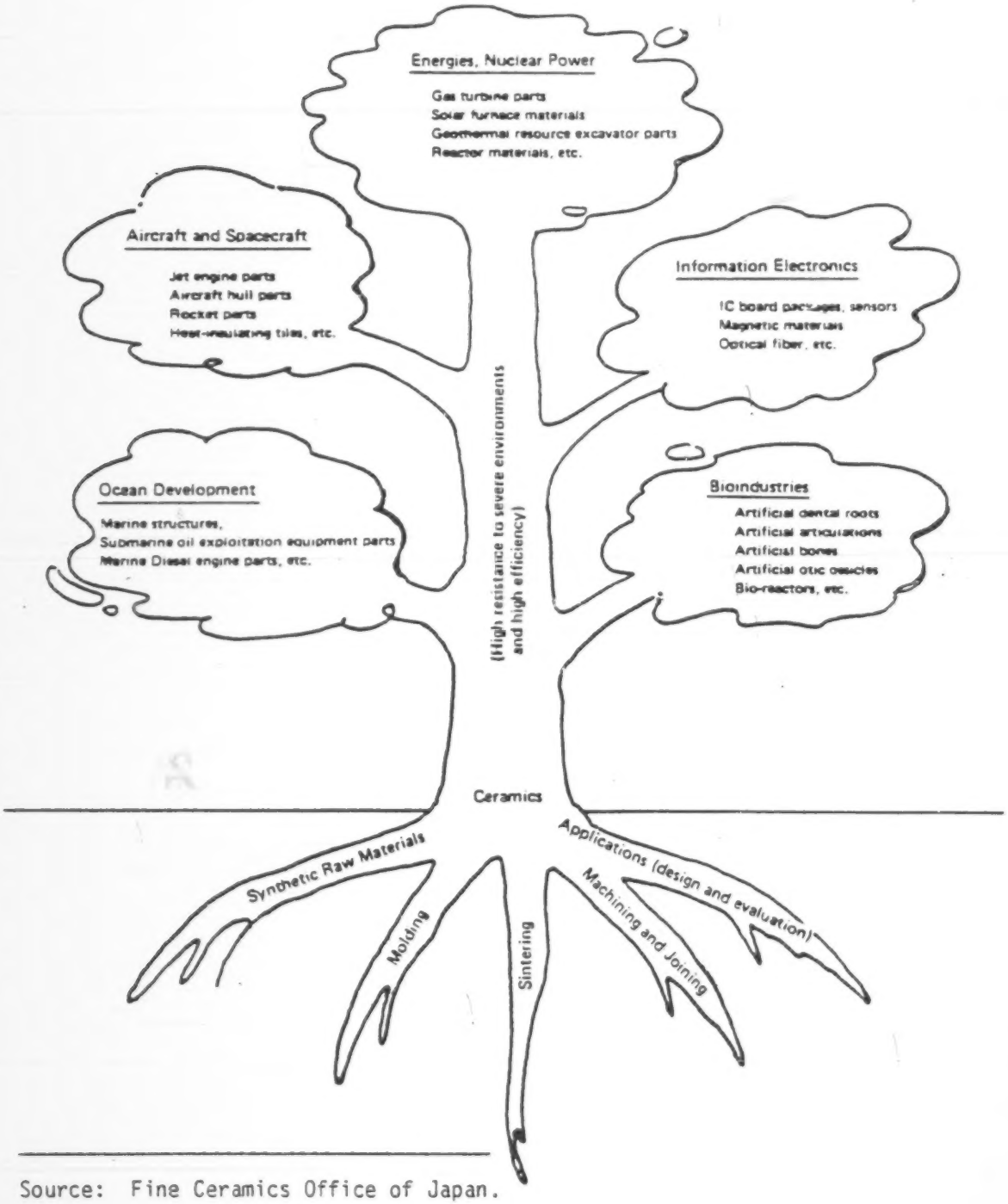
Appendix

AP.1 Outline of Production Processes of Fine Ceramics
AP.2 Production of Silicon Nitride
AP.3 Alumina Production Techniques
AP.4 Schematic Flow Diagram Showing PSZ Powder Processing Route

1. EXECUTIVE SUMMARY

The potential substitutability of advanced ceramics for strategic materials (chromium, cobalt, manganese, and platinum-group metals) in critical applications has been investigated. Advanced ceramic materials have the potential for substantial market share penetration in a broad range of critical applications. It is important to recognize that advanced ceramics is an emerging technology with a very broad base of current and potential applications, Table 1.1. However, it is difficult to precisely quantify the future impact of advanced ceramics. The technical potential of advanced ceramics is well recognized and the overall economic motivation is clear. It is this potential for performance, cost, and energy efficiency advantages which is currently driving the continuing development and growth of the existing $4 billion market for advanced ceramics. The results of ongoing research and development efforts continue to advance the state of this technology and its market potential. In many applications, advanced ceramics represent a technology leverage point which provides a foundation for advances in other high technology electronic, biological, power generation, production, and transportation systems. Consequently, efforts to advance the basic science and technology of advanced ceramics for critical applications will also aid other applications efforts and vice versa.

Table 1.1. Advanced Ceramics Supporting High Tech Industries for 1990's.



Source: Fine Ceramics Office of Japan.

A summary of the potential of advanced ceramics to substitute for strategic materials in critical applications is presented in Table 1.2 which includes (1) near term uses: cutting tool tips, wear parts, heat exchangers, some heat engine components, and (2) long term applications. Each application is considered with respect to the ceramic material to be used and its degree of substitution for chromium; cobalt, manganese, or platinum. The advantages of advanced ceramics usage and the factors affecting their implementation, as well as the extent of current commercialization, are also presented.

Near term uses of advanced ceramics can be grouped into two major categories; those requiring good wear resistance and those requiring high temperature durability. Wear resistant applications provide the greatest opportunity for ceramics use. Applications include cutting tool tips, seals, bearings, nozzles, etc. Only the first two applications are included in the table due to their greater degree of commercialization. Ceramics usage in wear applications primarily replace the cobalt used as a binder in cemented carbides. However, even at a high degree of market penetration, less than 5% of current cobalt consumption would be replaced. While increased fracture toughness is desireable, there are no significant technical barrier to ceramics usage in these applications. With current processing techniques, advanced ceramics appear to be cost competitive with cobalt-cemented tungsten carbide. Progress in ceramics processing technology should further improve the cost competitive position of these materials. Currenty,

Table 1.2. Potential of Advanced Ceramics to Substitute for Strategic Materials In Critical Applications.***

Near Term (before 1995)

Application	Ceramic Material	Potential* Strategic Material Saving	Advantage to Use of Ceramics	Factors Affecting Adoption			Extent of Current Commercialization US and World
				Technical	Economic**	Institutional***	
Cutting Tool Tips	Alumina Silicon Nitride Sialon	Cobalt; used as binder in tungsten carbide 2% Co savings if 20% market penetration	increased productivity	fracture toughness	Appears competitive with tungsten carbide	Lack of information within machinery tool industry	2% of US market Higher in Japan and West Germany
Wear Parts Pump Seals and Other Applications	Alumina-Zirconia Silicon Carbide	Cobalt; used as binder in tungsten carbide <1% of 80% market penetration	improved wear resistance and corrosion resistance	no significant barriers standardization of parts	Competitive with tungsten carbide except large <8 in. dia. seals.	Consumer awareness and lack of desire to change. Pumps are a replacement parts market, longer seal life is not seen as an advantage to producers.	20% of US and World market

* Potential strategic material savings are "best estimates"

** Factors listed in the economic and institutional barriers section apply to many of the potential applications for ceramics

*** These tables are not meant to be all inclusive but represent the key potential applications

Table 1.2. Potential of Advanced Ceramics to Substitute for Strategic Materials In Critical Applications.***(cont'd)

Near Term (before 1995)

Application	Ceramic Material	Potential* Strategic Material Saving	Advantage to Use of Ceramics	Factors Affecting Adoption: Technical	Economic**	Institutional***	Extent of Current Commercialization US and World
Heat exhangers Large Industrial Small single burner recoperators Heat engines	Silicon Carbide Cordierite Lithium Aluminum Silicate	Chromium used in high temperature stainless steels. Some manganese and cobalt % difficult to determine	Energy savings, longer furnace lives	Joining technology ceramic/ ceramic ceramic/ metal reproducibility of SiC tubes	higher initial capital investment than metallic heat exchangers high cost of SiC tubing	current depressed state of the domestic steel industry and metal processing industries. Change over to electrical induction heating which does not use recuperators	<5% of the US market Possibly higher in Japan
Turbochargers	Silicon Carbide Silicon Nitride	Chromium and Cobalt used in high temperature steels ~2% if 50% market penetration	higher temperature capability potential lower cost lower mass	ceramic/ metal joining and reproducibility of the ceramic rotors	Current cost of producing the ceramic rotor is high. Economies of scale are predicted	This is a new application. Ceramics will be used if they demonstrate superior performance	<1% of the US, Japan and European market. Before 1990 should see a large degree of market penetration

* Potential strategic material savings are "best estimates"

** Factors listed in the economic and institutional barriers section apply to many of the potential applications for ceramics

*** These tables are not meant to be all inclusive but represent the key potential applications

Table 1.2. Potential of Advanced Ceramics to Substitute for Strategic Materials In Critical Applications.***(cont'd)

Long Term (before 2010)

Application	Ceramic Material	Potential* Strategic Material Saving	Advantage to Use of Ceramics	Factors Affecting Adoption			Extent of Current Commercialization US and World
				Technical	Economic**	Institutional***	
Heat Engine Application Diesel Cylinders Pistons Sensors	Silicon Silicon Carbide Silicon Nitride ZrO_2, ZnO	Chromium and Cobalt in heat resistant and speciality steels. Up to 5% platinum group in catalytic converter. Up to 15% with 50% market penetration	Higher efficiencies potential for an 'adiabatic' diesel light weight engine components	fracture toughness reproducibility and reliability of parts	currently only prototype parts are produced, these are generally hot pressed and require diamond machining. They are expensive mass production and new processing techniques. Should generate significant economies of scale	ceramics require different designs. An almost revolutionary change in engine style is required to fully realize ceramics potential	<1% several demonstration engines have been in operation

* Potential strategic material savings are "best estimates"

** Factors listed in the economic and institutional barriers section apply to many of the potential applications for ceramics

*** These tables are not meant to be all inclusive but represent the key potential applications

Table 1.2. Potential of Advanced Ceramics to Substitute for Strategic Materials In Critical Applications.***(cont'd)

Long Term (before 2010)

Application	Ceramic Material	Potential* Strategic Material Saving	Advantage to Use of Ceramics	Factors Affecting Adoption			Extent of Current Commercialization US and World
				Technical	Economic**	Institutional***	
Gas Turbine Combustors Shrouds Rotors	Silicon Carbide Silicon Nitride SiAlON Lithium Aluminum Silicate	up to 5% Chromium Cobalt and 2% Maganese due to the elimination of high temperature steels. Up to 15% Platinum group metals. All assuming a 50% market penetration	Higher efficiencies ability to burn any fuel. Lower mass potentially lower cost.	Fracture toughness. Thermal shock resistance reproducibility and reliability	Only prototype parts which are expensive	Demonstration programs have focussed on the turbine rotor which may not be the ideal ceramic component. Failures in this arena have led to the rejection of ceramics for other more suitable parts.	<1% only prototypes and demonstration testing

* Potential strategic material savings are "best estimates"

** Factors listed in the economic and institutional barriers section apply to many of the potential applications for ceramics

*** These tables are not meant to be all inclusive but represent the key potential applications

ceramics share of the domestic cutting tool and mechanical seal markets is approximately 2% and 20% respectively.

Heat resistant applications of ceramics in the near term include heat exchangers and some diesel engine components. In these applications silicon carbide, silicon nitride, and aluminum silicates can replace heat resistant steels and alloys containing chromium, cobalt, and manganese. The overall precentage of these metals replaced is small, less than 5%. However, ceramics do provide major benefits in terms of energy savings, higher temperature capabilities, and weight reductions.

The factors affecting ceramics adoption in heat resistant applications are technical, economic, and institutional. A major technical obstacle to the use of ceramic is inadequate technology and experience in ceramic/ceramic and ceramic/metal joining. Although much progress has been made in this area, current technology limits the temperature capabilities and structural integrity of the part. Ceramics are presently much higher in cost than the metals they could replace, but programs to reduce the cost of SiC tubing for example, for industrial heat exchangers, are underway. The Gas Research Institute is funding work in this area and the initial results are encouraging. Other cordierite-based, heat exchangers are competitive for single burner recuperators when energy savings are taken into account. With mass production, economies of scale should reduce the component cost of diesel parts which are not currently cost competitive.

Institutional barriers to ceramics use in near term applications include a lack of consumer awareness, education, and willingness to try new materials. The domestic ceramic community also lacks the concentration and coordination of other materials communities with which it must compete. In addition, there is also a lack of knowledge of proper design with ceramics which emphasizes a larger barrier, the need for innovative design to more fully utilize the special properties of advanced ceramics. Designers are often unaware of, or have insufficient data to design with advanced ceramic materials. A data bank of materials properties as well as a standardization of "expected" properties from manufacturers is needed to encourage advanced ceramics usage. Another problem has been the depressed state of the economy. High initial capital outlays for equipment such as large industrial ceramic heat exchanger systems have slowed commercialization even though the domestic industry could benefit from the associated energy savings.

It is difficult to predict the future, however, two specific applications are listed in Table 1.2 for ceramics use in the long run. As energy costs rise and the availability of present day fuels fluctuates, new engine technologies with greater thermal efficiencies and multiple fuel capabilities will evolve. Due to their higher temperature capabilities, resistance to corrosive environments, low inertial mass, ready availability of raw materials, and potentially low cost, ceramics should become an integral part of new power generating technology. In order for ceramics to be used in these applications, a number of technical

barriers must be overcome. Higher fracture toughness, high temperature strength, and good thermal shock resistance are crucial to these applications. Ceramic materials for engine applications capable of being reproducibly and reliably produced, something which is not possible at the current state of technology.

Economic barriers to commercialization of ceramic engine components are large, and it is not a simple task to estimate future costs of producing actual components. The current technology is at only the prototype or possibly pilot plant stage and only very small volumes of component parts have been produced. A full scale production facility to mass produce advanced heat engine components is not yet in operation. Ceramic raw materials are inexpensive. However, a large investment in capital equipment, energy, and skilled labor is required to produce an advanced ceramic component. At the present time, rejection rates on components are high (as high as 75% in some applications), and parts require extensive finishing operations. In the future, as new processing technology developments are made in both the powder production and forming stages, many of the costs of producing a ceramic component may be reduced.

Institutional barriers for long range ceramics utilization are greater than those for the near term. Domestic companies have been slow to invest in new ceramic ventures and development programs which has not been the case in Japan. Many of the government funded programs have been directed at a particular application, such as the gas turbine engine. These demonstration programs have been designed

to show that ceramics can be used, for example, as turbine rotors. This is not the ideal application for advanced ceramics due to a number of engineering constraints. However, if the present day ceramic does not meet the full requirements for this and other applications which are pushing the state-of-the-art, overall usage in general may suffer. This method of funding neglects applications that are less demanding and more attractive for ceramic materials, and has put too little emphasis on process development, testing, and basic science. In addition, ceramics cannot generally be used as a direct substitute for a metal component. Design for and with ceramics is required to maximize the potential benefits. This design function will require education or re-education on the part of design engineers.

In summary, ceramics have excellent potential in a number of applications which would have a significant impact on critical materials usage. Ceramics will penetrate the various markets previously mentioned first through wear resistance and heat resistance and then, potentially, high temperature strength. Progress has been made toward reducing the technical barriers in a number of applications. Economic barriers may be reduced through larger volume production and the associated economies of scale. The institutional barriers, though large, are not insurmountable if effort is applied in the appropriate direction. Advanced ceramics will probably not replace large portions of U.S. demand for critical materials. However, their properties could be used to benefit many processing industry users. Higher energy efficiencies, longer

equipment life, higher productivity in a number of areas, and many added benefits in high temperature metals processing and chemical processing industries represent the greatest potential for ceramics. In order for both potential strategic and industrial applications to become a reality, ceramic producer, user, and government research and development efforts must be concentrated, coordinated, and forthcoming. The danger of hesitating with the development of advanced ceramic technology is becoming dependent on others for this technology, probably Japan, and thereby simply shifting strategic dependencies.

2. DEFINITION OF CERAMICS

Ceramic materials include all chemically inorganic materials except metals[1] and are generally processed at high temperatures before use. Usually, the semiconductors germanium (Ge) and silicon (Si) are excluded. Ceramics are compounds or solid solutions which may be either ionically and covalently bonded.[2] Ceramic crystals are formed by either electrostatic attractive forces, electron pair sharing between atoms, or a combination of both.

Ceramic materials have many characteristics which distinguish them from metals. Ceramics are generally more stable chemically and thermally and are better insulators than metals. They are much stronger in compression than in tension and do not have the same ductility, or "forgiving" nature, of a metallically bonded structure. On the other hand, ceramics are harder, more rigid, and more stable at high temperatures than either metals or polymers. Ceramics are used in a wide range of applications, both in conjunction with polymers and metals and as substitutes for these materials.

There are currently two broad classes of ceramic applications: traditional and high technology. The major traditional uses of ceramics, listed in Table 2.1, include cement, glass products, structural clay products, abrasives, and refractories (or heat resistant ceramics). The value of traditional ceramic shipments, as reported in the 1977 census of manufacturers, is approximately $25.4 billion.[3] Advanced ceramics are used in a number of electronic, magnetic, optical, thermal, mechanical, biological, and chemical

Table 2.1. U.S. Ceramic Market Data.[3]

Industry	Estimated Shipments at Manufacturers' Level, 1977
Cement+	$ 3,960,000,000
Flat Glass+	1,560,000,000
Glass Containers+	5,075,000,000
Fibrous Glass*	2,008,854,000
Consumer, Scientific, Technical, Industrial & Table Glass*	2,429,446,000
Floor & Wall Tile*	311,802,000
Vitreous Plumbing Fixtures+	520,000,000
Vitreous China Food Utensils & Earthenware Food Utensils**	252,000,000
Porcelain Electrical Supplies**	367,500,000
Pottery Products Not Classified Elsewhere*	229,900,000
Electronic/Industrial & Newer Ceramics**	2,500,000,000
Porcelain Enamel, Metal Stamping, Stove Equipment, Domestic Laundry Parts, Refrigeration Machinery Parts, Signs, Sanitaryware, Furniture, Housing & Industrial	1,250,000,000
Brick & Structural Clay Tile+	682,000,000
Vitrified Clay Sewer Pipe & Fittings*	107,657,000
Clay Refractories*	789,249,000
Nonclay Refractories*	1,060,625,000
Refractory Materials Not Classified Elsewhere*	400,000,000
Abrasives**	1,955,800,000
Flower Pots#	10,000,000
Total	$ 25,418,833,000

* Current Dept. of Commerce figures.
** Based on 1977 Census of Manufacturers, U.S. Dept. of Commerce
# Based on figures supplied by Porcelain Enamel Institute
+ 1983 U.S. Industrial Outlook, Dept. of Commerce

applications. High technology ceramics are sometimes refered to as advanced ceramics. Structured ceramics are a subclass of advanced ceramics which are used in structural applications. This type of ceramics had shipments valued at $2.5 billion in 1977. However, this segment of the market is growing as new uses for the high temperature, high wear-resistant, electromagnetic, and mechanical properties of these new ceramics develop and expand. Fine structural ceramics are now being developed for heat engines, wear parts, cutting tools, and other applications to substitute for high temperature specialty steels and superalloys which are based upon the use of expensive imported and strategic metals. A partial listing of industrial applications, properties, and functions of advanced ceramics is provided in Table 2.2.

The current market value for advanced ceramics is summarized in Table 2.3. At the present time, the structural portion of this world market is only $250 million. With improved processing of powders, refined manufacturing techniques, and wider structural uses (for example, in heat engines), an enormous market potential is available. The future of the new high technology ceramics industry, which could represent a $20 billion world market by the year 2000[3], or a $10 billion domestic market, will depend upon the development of a technology that can produce ceramics reliably, reproducibly, and at a cost competitive with other existing materials technologies.[5]

Table 2.2. Industrial Functions of Fine Ceramics.[14]

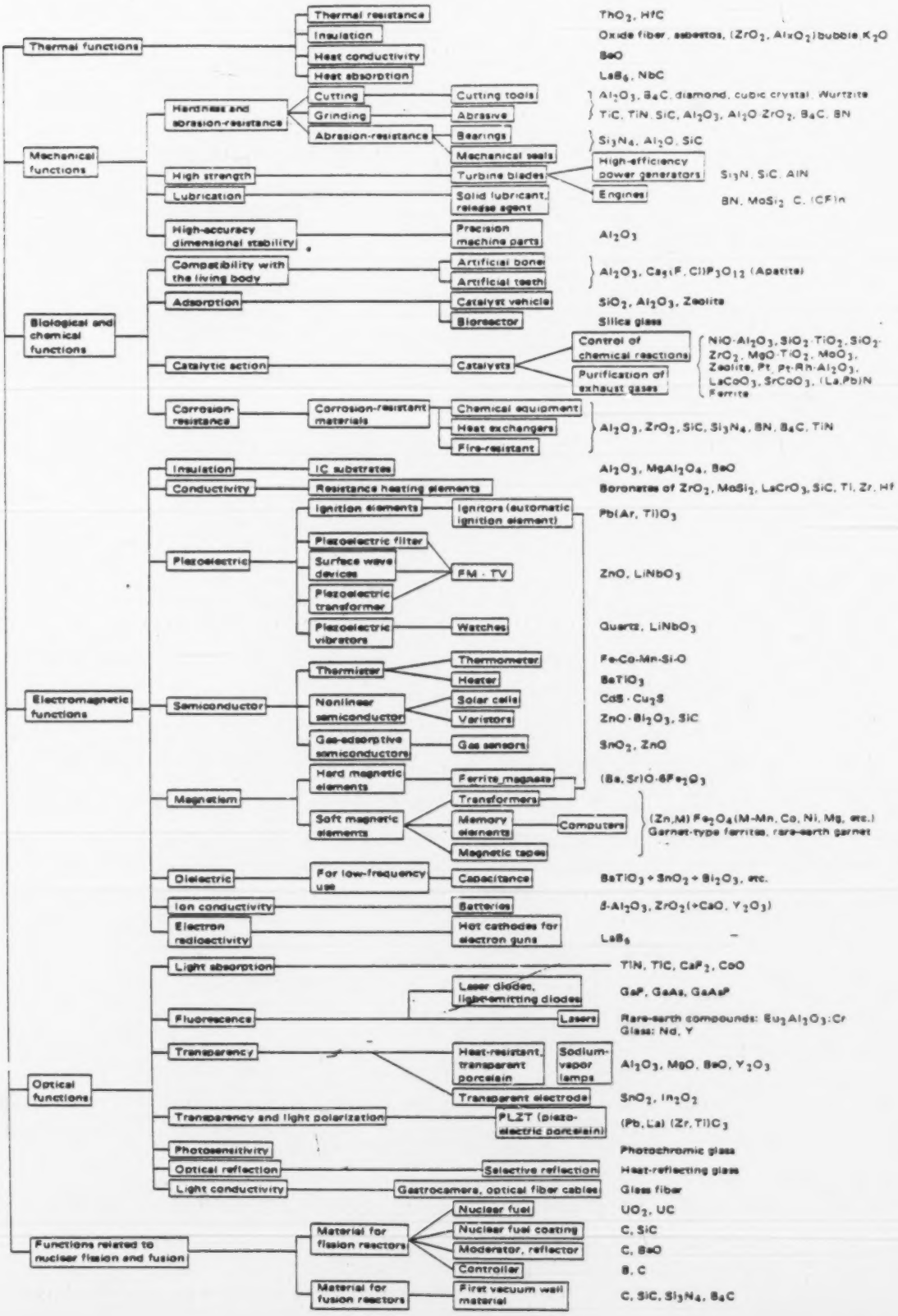


Table 2.3. High Technology Ceramics Markets (1980 - $M)*+

Product	Japan	World
Ceramic Powders	$130	$250
Electronic IC Packages/Substrates	540	880
Capacitors	325	750
Piezoelectrics	155	185
Thermistor/Varistors	125	200
Ferrites	380	480
Gas//Humidity Sensors	5	45
Translucent Ceramics	20	45
Cutting Tools: carbide, cermet, coated	120	1,000
non-carbide**	5	25
Structural Ceramics (heat and wear resistant)	120	250
Totals	$1,925M	$4,110M

* Excludes fibers, nuclear fuels, spark plugs

** For example, alumina, partially stabilized zirconia, silicon carbide and nitride, and oxynides.

+ Adapted from Reference No. 4.

Properties and Applications

A general classification of ceramics by function and the ceramic materials used in high tech applications is given in Table 2.4. Potential substitutes for critical materials are also indicated. Because a great number of materials are classified as ceramics, a wide variety of properties are available.[4] Ceramics have thermal, mechanical, electrical, magnetic, and chemical properties which set them apart from other materials. The thermal properties of many ceramics provide good thermal insulation while others exhibit high thermal conductivity. Thermal expansion varies with the specific ceramic material, from an extremely small expansion coefficient to one almost as high as that of cast iron. The thermal shock resistance of ceramics, which is controlled by the Young's modulus, the expansion coefficient, and strength, is very good. Some ceramics can withstand rapid temperature changes of more than 500°C.

The mechanical properties of ceramics typically include high stiffness and rigidity. However, due to the nature of the atomic bonding, ceramics are brittle; thus, when mechanically loaded (stressed), they do not readily deform (strain). Ceramics are extremely strong in compression, but are not tough. This lack of toughness, the measure of fracture resistance, has limited the direct substitution of ceramics for metal parts. If flaws or cracks in the structure exist, tensile loads lead to crack propagation and catastrophic failure. This has been the major barrier to the expanded use of ceramics in a wide range of applications.

Table 2.4. Classification of High Tech Ceramics by Function With Possible Areas of Substitution for Strategic Metals.*

Function	Material	Applications	Examples of Areas of Possible Substitions
Electric	Insulating (Al_2O_3, BeO, MgO)	IC circuit substrate, package, wiring substrate, resistor substrate, electronics interconnection substrate	
	Low firing and/or glass ceramics, ferroelectrics ($BaTiO_3$, $SrTiO_3$)	Ceramic capacitor	Direct ceramic for Ta capacitors; Indirectly by low temperature firing use Cu for W, Mo or Pt-group wires; Ni for Pt-group electrodes.
	Piezoelectric (PZT)	Vibrator, oscillator, filter, etc. Transducer, ultrasonic humidifier, piezoelectric spark generator, etc.	
	Semiconductor ($BaTiO_3$, SiC, $ZnO-Bi_2O_3$, V_2O_5, and other transition metal oxides	**NTC thermistor:** temperature sensor, temperature compensation, etc. **PTC thermistor:** heater element, switch, temperature compensation, etc. **CTR thermistor:** heat sensor element **Thick film thermistor:** infrared sensor **Varistor:** noise elimination, surge current absorber, lighting arrestor, etc. **Sintered CdS material:** solar cell **SiC heater:** electric furnace heater, miniature heater, etc.	Pt, Pt-Rh heaters, Ni-chrome heaters

Table 2.4. Classification of High Tech Ceramics by Function With Possible Areas of Substitution for Strategic Metals. (cont'd)

Function	Material	Applications	Examples of Areas of Possible Substition
Electric	Ion conducting (β-Al_2O_3, ZrO_2)	**Solid electrolyte for sodium battery** **ZrO_2 ceramics:** oxygen sensor, pH meter fuel cells	
Magnetic	Soft ferrite	Magnetic recording head, temperature sensor, etc.	Ceramics for Co, Sn magnets
	Hard ferrite	Ferrite magnet, fractional horse power motor, powders for tapes and disks (δ-Fe_2O_3, CrO_2)	Ceramics for AlNiCo magnets
Optical	Translucent alumina	High pressure sodium vapor lamp	
	Translucent magnesium oxides, mullite, etc.	For a lighting tube, special purpose lamp, infrared transmission window materials	
	Translucent Y_2O_3-ThO_2 ceramics	Laser material	
	PLZT ceramics	Light memory element, video display and storage system, light modulation element light shutter, light valve	
Chemical	Gas sensor (ZnO, Fe_2O_3, SnO_2)	Gas leakage alarm, automatic ventilation fan; hydrocarbon, fluorocarbon detectors, etc.	Reduced use of Pt-group catalyst
	Humidity sensor ($MgCr_2O_4$-TiO_2)	Cooking control element in microwave oven, etc.	

Table 2.4. Classification of High Tech Ceramics by Function With Possible Areas of Substitution for Strategic Metals.*

Function	Material	Applications	Examples of Areas of Possible Substition
Chemical	Catalyst carrier (cordierite)	Catalyst carrier for emission control	
	Organic catalyst	Enzyme carrier, zeolites, other ceramics	Catalytic processes may replace Co, Pt
	Electrodes (titanates, sulfides, borides)	Electrowinning aluminum, photochemical processes, chlorine production	
Thermal	ZrO_2-based Al_2O_3-based Si-based	Infrared radiator, thermal barrier coatings	Reduced use of W, Cr, Co, Ni
Mechanical	Cutting tools (Al_2O_3, TiC, TiN, others)	Ceramic tool, sintered SBN Cermet tool, artificial diamond Nitride tool	WC-Co cemented cutting tools and high-speed steels
	Wear resistant (Al_2O_3, ZrO_2)	Mechanical seal, ceramic liner, bearings, thread guide, pressure sensors	Hard facing alloys (Cr, Co, Mn)
	Heat resistant (SiC, Al_2O_3, Si_3N_4, ZrO_2, others)	Ceramic engine, turbine blade, heat exchangers, welding burner nozzle, high frequency combustion crucibles	Superalloys (Co, Cr, Mn)

Table 2.4. Classification of High Tech Ceramics by Function With Possible Areas of Substitution for Strategic Metals.*

Function	Material	Applications	Examples of Areas of Possible Substition
Biological	Alumina ceramics implantation	Artificial tooth root, bone, and joint	Bone and tooth implants (Pt, Co, Cr-based)
	Hydroxyapatite bioglass	"	
Nuclear	(UO_2, UO_2-PuO_2)	Nuclear fuels	Specialty alloys
	Cladding material(C, SiC, B_4C)		(Cr, Co, Mn)
	Shielding (SiC, Al_2O_3, C, B_4C)	Glass and ceramic encapsulation of spent fuel	Stainless steel (Cr, Mn)

* Compiled from Reference 4.

Any ceramic part is only as strong as its largest flaw (Griffith Crack Theory[2]). Monolithic ceramics (or those cast as a single piece) require new and improved processing techniques to reduce flaw size and flaw population. Greater control of powder processing parameters will use homogeneous powders, producing homogeneous greenware (prefired parts), and yielding a final component with fewer or no critical flaws. This will increase both the performance and the reliability of ceramic components. Controlled process parameters will also add greater reproducibility to the final components.

Ceramic coatings, used on metallic parts, combine high temperature capabilities or wear resistance of the ceramic with the ductility of the metal matrix. Ceramic/ceramic composites also attempt to increase the toughness of existing ceramics.

Structural ceramic parts will be used first in applications which do not require high tensile strengths. Small, stationary parts which either insulate or provide wear or corrosion protection are also excellent first uses for ceramics. As the technology matures producing tougher, more fracture-resistance ceramics, larger and moving parts will become feasible.

Processing Ceramics

The production of most ceramics, including traditional and high tech ceramic components, consists of the following four basic processing steps, a) powder preparation (including raw material selection and powder production), (b) forming, c) sintering, and

d) finisning. The various components of each of these processing steps, outlined in Table 2.5, are discussed below.

Powder Preparation

Raw Material Selection. Ceramic raw materials are generally more readily available and less expensive than the critical materials used in specialty steels and superalloys. Many minerals which serve as the raw materials of ceramics are abundantly available in the earth's crust. Silica, zircon, flint, clay, and feldspar are found in numerous locations throughout the world, including the United States. But some ceramic materials, such as chromite and alumina minerals, are not available domestically and must be imported. While there are many worldwide sources of alumina, major sources of chromite include South Africa, USSR, and Albania. The United States' supplies of chromite are low grade and are presently not economical to mine.

Clay, silica, and feldspar are the principal raw materials used in the production of traditional ceramics. Combined with a spectrum of other materials, they generate a whole range of properties. These materials are used in most whiteware products, wall and floor tiles, triaxial and nontriaxial porcelains, glasses, glazes, enamels, refractories, and advanced ceramics. Table 2.6 provides a list of these materials and their uses.

The differences between traditional and high technology ceramics is due in part to the raw materials used. Clays and many of the non-clay minerals are associated with traditional ceramics

Table 2.5. Production Techniques for Fine Ceramics.[6]

Technique	Method	Examples
Powder Synthesis	Al_2O_3 - Bayer process, calcining $Al(OH)_3$	$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$ $NaAl_2O_2 + 2H_2O \rightarrow NaOH + Al(OH)_3$ $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$
	$BaTiO_3$ - Calcine barium carbonate with titania	$BaCO_2 + TiO_2 \rightarrow BaTiO_3 + CO\uparrow$
	MgO - Brine or Seawater reduction	$Mg(OH)_2 \rightarrow MgO + H_2O$
	MgO - Calcine magnesium carbonate	$MgCO_3 \rightarrow MgO + CO_2$
	SiC - SiO_2 Reduction	$SiO_2 + C \rightarrow SiC + O_2$
	Si_3N_4 - Direct nitriding	$3Si(metal) + 2N_2 \rightarrow Si_3N_4$
	ZrO_2 - Calcining of zircon sands	$ZrSiO_4 \rightarrow ZrO_2 + SiO_2$ $ZrSiO_4 + Na_2CO_3 + K_2CO_3$ → alkali zirconium silicate → alkali zirconate + alkali silicate → $ZrOCl_2 \cdot 2H_2O$ $ZrO \cdot Cl_2 + 2HCl + NH_4OH \rightarrow$ $Zr(OH)_2 \rightarrow ZrO_2 + H_2O$
Crushing		
Granulating		
Blending		
Mixing		
Forming	Slip casting	Artware; thin, uniform-walled shapes
	Dry pressing	Cutting tools, sanitary ware, refractories
	Extrusion	Bricks, tubing, honeycomb structures
	Injection molding	Turbocharger rotors, glow plugs
	Tape casting	Ceramic capacitors
	Melting/casting	Glass, fuse cast refractories

Table 2.5. Production Techniques for Fine Ceramics (cont'd).[6]

Technique	Method	Examples
Sintering	Pressure sintering	Al_2O_3, MgO, $BaTiO_3$
	Reaction bonding	Si_3N_4
	Hot pressing (HP)	Si_3N_4, SiC, BN
	Hot isostatic pressing (HIP)	Si_3N_4, SiC
Coating	Slurry	Porcelain enamels
	Plasma, flame sprayed	Thermal barrier coatings, Al_2O_3, ZrO_2, CrO_2
	Sputtering	Si_3N_4 on Si-IC's
	Chemical vapor deposition	SnO_2 transparent electrodes
	Physical vapor deposition	Thin films
Fiber/Whisker Production	Polymer pyrolysis	SiC, graphite
	Rice hulls	SiC
Single Crystal Production	Solution	Magnetic bubble memories (garnet)
	Melting	Substrate of Si on sapphire
	Hydrothermal	Quartz
Finishing	Mechanical	Diamond grinding, cutting, piercing
	Chemical	Etching
	Radiation	Laser, electron beam, ion beam, spark
	Electric	Electric discharge

Table 2.5. Production Techniques for Fine Ceramics (cont'd).[6]

Technique	Method	Examples
Joining	Ceramic/metal	Mechanical, brazing, epoxy
	Ceramic/ceramic	Diffusion, mechanical, brazing, epoxy

Table 2.6. Traditional Ceramic Materials and Their Uses.[1]

Material	Uses
Clays	
Kaolin	Whitewares, porcelain, and china bodies.
Ball	Pottery, sanitary ware, floor and wall tile, china, electric porcelain, other.
Fire	Refractories, refractory mortars, ramming mix.
China	China and whitewares.
Slip	Glazing stoneware, electrical porcelain.
Bentonite	Increases plasticity and dry strength of unfired ware.
Pottery	Pottery, porcelain, and china.
Others (e.g. shales, mudstone)	Sewer pipes, bricks.
Non-Clay Materials	
Silica	Glass, fused silica, refractories, whiteware, glazes.
Feldspar	Glass, pottery.
Nepheline syenite	Feldspar substitute, glass.
Lime	Refractories, glass.
Magnesite	Whitewares, glazes, enamels, glass, and refractories.
Dolomite	Whitewares, glass, refractories.
Gypsum	Plaster of paris.
Chromite	Refractories for metallurgical and chemical use.
Aluminum silicates	Refractories, spark plugs, pyrometer tubes, mullite refractories for metallurgical and glass industry.
Pyrophyllite	Whitewares, floor and wall tile, refractories, cement and filler.
Magnesium silicates	Saggers, kiln furniture, low temperature insulating refractories, self lubricating.
Fluxing minerals	Glass, glazes, enamels.
Refractory minerals	High temperature applications, refractories, heating elements.

Table 2.6. Traditional Ceramic Materials and Their Uses (cont'd).[1]

Material	Uses
Special Materials	
Carbides Borides Nitrides	Super refractories, high temperature use, low volatility
Sulfides	CeS, ThS crucibles, <1800°C.
High Purity	
Single oxides	Enhanced refractory properties.
Complex oxides	Ferrites, titanates.
Nuclear ceramics	UO_2 - fuel.

and are not generally used in newer advanced ceramics. However, some materials such as alumina (Al_2O_3), zirconia (ZrO_2), and silicon carbide (SiC), have both traditional and high tech applications. The ability of these materials to fulfill both roles is a function of powder preparation and manufacturing techniques. Careful processing of existing materials imparts the higher purity, strength and reproducibility required for new applications.

Powder Production. Ceramic powders are processed from naturally occurring minerals, by-products of mining operations, or chemical reactions. Powders are traditionally classified on the basis of chemical composition, particle size, particle size distribution, and properties related to their firing behavior, and shrinkage, as listed Table 2.7. Powder production for advanced ceramics has become an increasingly critical step. Purity, particle size, particle shape, particle size distribution, and agglomeration are extremely important and must be controlled to produce reliable, reproducible components.

Traditional ceramic powders are produced by one of a number of chemical processing techniques. Powders such as alumina, silica, magnesia, calcia, and zirconia are derived from naturally occurring minerals or sands, which are heat treated, leached, or reacted to remove water and impurities. Powder production for advanced ceramics utilizes much the same processes; however, more care is taken to insure purity and powder uniformity. High tech powders often require a high surface area to volume ratio. New techniques such as sol-gel, co-precipitation, and laser synthesis have also

Table 2.7. Properties of Aluminas Used in Fine Ceramics.[7]

Characteristic	Type of alumina					
Number	A-2	A-3	A-5	A-10	A-14	T-61
Characteristic	Calcined	Calcined	Calcined	Low soda	Low soda	Tabular alpha
Al_2O_3, %	98.9	99.2	99.2	99.5	99.6	99.5+
SiO_2, %	0.02	0.02	0.02	0.08	0.12	0.06
Fe_2O_3, %	0.03	0.03	0.03	0.03	0.03	0.06
Na_2O, %	0.45	0.45	0.50	0.2	0.04	0.02
Ignition loss, %	0.6	0.4	0.2	0.3	0.3	0
Size analysis, cum, %						
On 100 m	4-15	4-15	2-10	4-15	4-15	
On 200 m	50-75	50-75	40-65	50-75	50-75	
On 325 m	88-98	88-98	75-95	88-98	88-98	
Through 325 m	2-12	2-12	5-25	2-12	2-12	
Bulk density, packed lb/ft^3	68	68	63	80	83	135
Firing shrinkage, linear %	19-23	20-22	16-18	14-16	16-18	10

[a]Data in this table were supplied by the Aluminum Company of America. Similar products are made by Reynolds, Alcan, and Kaiser in the United States and firms in England, Germany, Japan, and France.

The calcined aluminas are used in bodies for high strength, good abrasion resistance, and chemical inertness. The low-soda aluminas are used in electrical bodies demanding a low loss factor. The tabular alumina is used in refractories and electrical insulators.

been developed to produce high purity, more uniform, and unagglomerated powders. Powder production techniques will be reviewed later in the Powder Supply section.

Traditional ceramic powders are ground, sieved, and sized in preparation for the forming process. Materials can be either wet- or dry-mixed. Dry mixing, though a less expensive process, is not applicable to a great number of products because it does not result in the required degree of homogeneity. Particle sizes and size distributions are critical in advanced ceramics to produce uniform green densities which result in high fired densities. Since ceramics are generally sintered rather than melted and atomic diffusion coefficients in ceramics are generally low, it is critical to achieve uniform, densely packed green structures at the powder packing stage so that rearrangement can occur to produce a fully dense, sintered, finished ceramic part.

Forming Processes

Ceramic raw materials must be formed and shaped before use. The forming process generally determines final ceramic properties. The processing variables in the forming step affect particle shape, particle packing and distribution, phase distribution, location of pores, shrinkage, and dry and fired strength.

Forming processes for ceramics, while many and varied, are generally classified as either cold or hot forming. Within each of these categories, the ceramic forming is accomplished by either plastic deformation operations such as extrusion, dry pressing, and

hot forming or by casting operations such as slip, fusion, or tape casting and injection molding. Cold forming techniques prepare shapes which may be machined before or after firing. The amount of homogeneity in cold formed greenware determines the extent and uniformity of shrinkage during firing. Hot forming methods combine into one step the forming and sintering operation to produce simple geometric shapes. Hot formed shapes must be machined to final product shape and specifications. Hot forming operations also include chemical or reaction-bonded coating techniques.

Cold Forming

The major cold forming methods include slip casting, extrusion, dry pressing, injection molding, tape casting, and many variations of these general methods. The majority of these processes have been adapted to or developed for high technology ceramics.

Slip Casting. Slip casting allows the fabrication of a wide range of shapes. The general slip casting process is shown in Figure 2.1. Ceramic particles are suspended with deflocculants in a liquid, forming a slip or slurry. Traditional slip castings are made in plaster of paris molds. Capillary action and/or pressure removes the liquid (usually water) from the slip through the mold walls. The dried greenware is removed from the mold for firing to final densities. Mold design and uniform dispersion of powders within the slip are critical for the creation of a uniform product.

Other casting techniques such as pressure casting are based on the same type of procedure. However, this technique relies on pressure instead of capillary action to remove water from the slip,

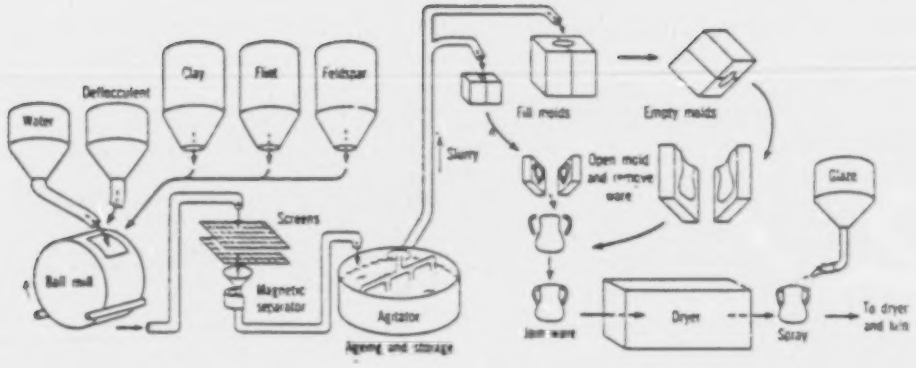


Figure 2.1. Simplified flow diagram of slip casting art ware.[1]

thereby avoiding the time constraining mold drying operations necessary for normal slip casting operations.

Extrusion. This technique, used for years to make traditional ceramics like refractories and bricks, see Figure 2.2, can easily be adapted to high performance ceramics. A malleable, plasticized mass is mixed, pugged, de-aired, and finally extruded. Plasticizers are generally added to non-plastic materials along with 12-20% liquid.[1] The extruded product is a strong, dense, plastic body. Shapes produced by this method include those with a fixed cross-section such as rods, bars, tubes, or even thin-walled, honeycombed structures. The process is fast, economical, and upon drying provides a strong pre-fired body.

Dry Pressing. A simple dry pressing operation is illustrated in Figure 2.3. Dry pressing operations generally produce refractories, whitewares, and abrasives. Powders are often combined with binders or plasticizers, placed in a cavity, and pressed from one direction (uniaxial press). The die cavity may be vibrated prior to pressing to give a more uniform powder distribution. Dry pressing is economical, but limited in use by size and shape restrictions. Dry pressed parts may be green-machined before firing.

A variation of the uniaxial dry pressing is isostatic pressing which is slightly more expensive but better suited for nigher quality parts or more intricate shapes. The powder within a pliable mold cavity is pressurized, creating a hydrostatic or isostatic

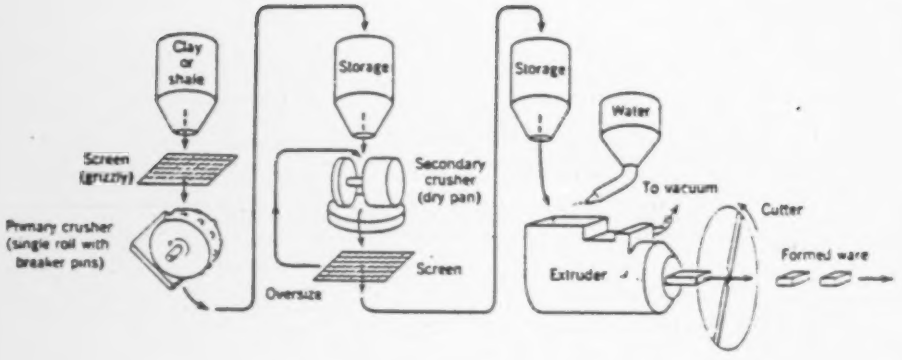


Figure 2.2. Simplified flow diagram of an extrusion process.[1]

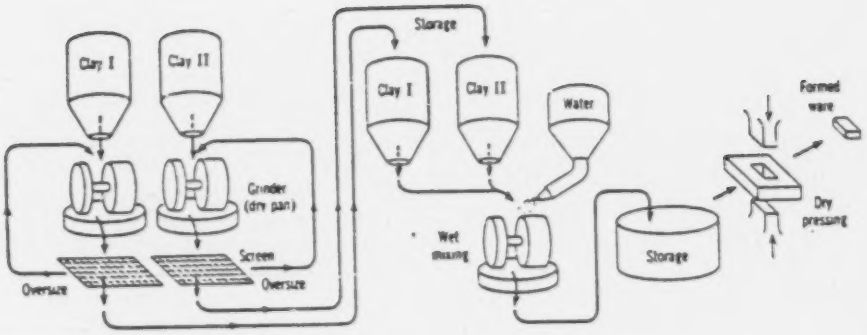


Figure 2.3. Simplified flow diagram of an operating dry pressing operation.[1]

pressure on the powder which results in a more uniform pressing operation.

Injection Molding. This technique has been developed from plastic molding techniques to provide an inexpensive, highly productive method for forming intricately shaped ceramic components. This process requires suspended powders in a liquid with a high powder volume/liquid ratio. Thermal or chemical changes in the liquid, usually resins or polymers, causes the body to become rigid after the mix is injected into the die cavity, usually under pressure. The piece is then removed, heated to burn out binders, and then sintered to high densities. Figure 2.4 is an illustration of a two stage screw plunger plastic molding machine, which is similar to equipment used in the injection molding production of ceramics.

A wide range of liquids have been used for the suspension. Powder volume/liquid ratios effect fluid flow; therefore, the powder must be compatible with the fluid phase. Fluid flow and variations in powder densities are critical to firing a defect free, part with the required tolerances. This process is ideally suited to the production of intricately shaped, dense components requiring a minimum of machining.

Other cold forming techniques exist;[1-2] however, the above provide an overview of typical techniques.

Sintering. Although sintering is not precisely a forming technique, it is a method for converting loosely bonded powder to a dense body. Ceramics generally melt at extremely high temperatures (much greater than 1000°C); others only sublime at even higher

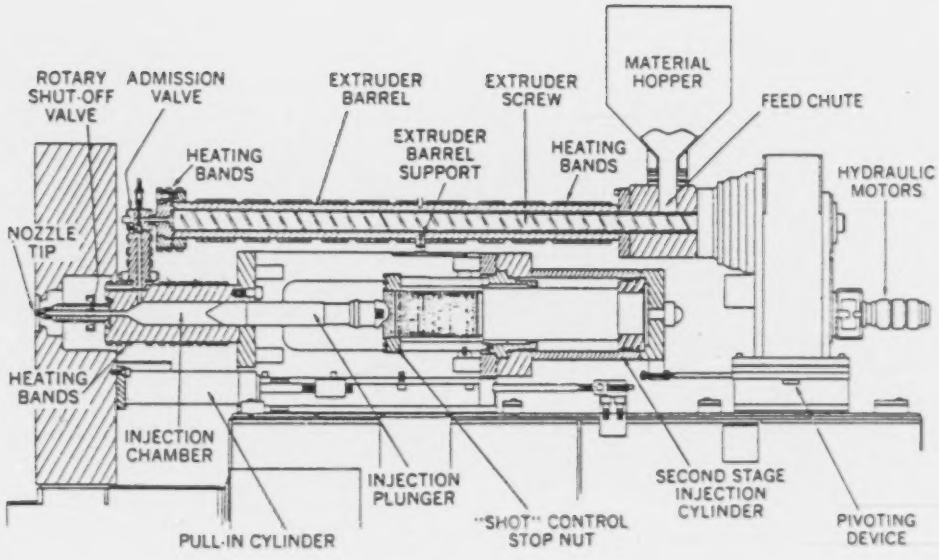


Figure 2.4. Schematic drawing of injection end of two-stage screw plunger machine.[9]

temperatures (Si_3N_4, 1900°C). These high temperatures and the fact that they have over twice the volume change upon solidification compared to metals requires that ceramics are sintered for most applications.

Sintering involves particle consolidation by diffusion on an atomic scale. Formed greenware is placed in a batch or continuous furnace or kiln and fired. Moisture and organics are first eliminated and then, at the temperature range where the appropriate diffusion processes occur, matter is moved from the particles into the void spaces between the particles, causing densification and resulting in snrinkage of the part. Sintering procedures combine theoretical models of diffusion with engineering practice. Combined with techniques like slip casting, it is an economic method for producing intricate ceramic components. Its drawback lies in the need to use additives and the long sintering times required to achieve high densities. Additives are used in ceramic processing to aid in sinterability. Because fine powders cannot be uniformly distributed in the casting or shaping operation, the particles are not optimally packed. Thus, sintering aids allow liquids to form which cause movement and rearrangement of the particles and increased diffusion of matter, often at lower temperatures. Additives often segregate to the grain boundaries or form grain boundary phases which can reduce the mechanical, electrical and high temperature properties of the final product. Voids may also be trapped within the grains or at tne boundaries, reducing final strength and density.

Hot Forming and Sintering

Hot forming methods include hot pressing, hot isostatic pressing, near-net shape processing, chemical/physical vapor deposition, and flame and plasma spray coatings. Hot forming operations combine the shaping and thermal processing stages, unlike cold forming processes which require separate heat treatment and forming operations.

Hot Pressing. Since the discovery that pressure as well as heat aids in the densification of ceramic ware, hot pressing has been used to fabricate fully dense ceramics. Hot pressing requires a high temperature die, often graphite, and a high temperature furnace (usually in a vacuum or inert atmosphere). Powders are dried and loaded into the die cavity. Heat and pressure (uniaxial) are then applied simultaneously to sinter the powder to maximum density. The ceramic properties possible with hot pressing are excellent. Unlike cold-pressed parts, hot pressed parts, due to their hardness, require expensive diamond machining to meet the finished part specifications. This process is not well suited to high volume production, requires expensive tooling, and is extremely limited in terms of final shape. The effect of pressure in hot pressing serves the same purpose as additives in sintering; it allows for re-packing of the particulates in the die cavity before matter is moved by atomic diffusion.

Hot Isostatic Pressing. This process, similar to hot pressing, applies pressure isostatically rather than unidirectionally. Hot isostatic pressing yields final parts which

have improved properties compared with those obtained from slip casting or dry pressing. The hot isostatic pressing operation is expensive and requires high production volumes for the tooling to be economical.

Near Net Shape Processing. Near net shape processing (NNSP) refers to any forming process, or combination of forming techniques, which produce a final product requiring a minimum of machining. NNSP also refers to the addition of nitrogen or silicon to a preformed part (nitriding or siliconizing). A formed piece is pre-sintered. Pre-sintering a part allows initial consolidation to occur and forms a strong porous microstructure. The pre-sintered part is then impregnated with silicon or nitrogen gas. The materials are reaction bonded to create a silicon nitride (Si_3N_4) or siliconized SiC part which is dense and approximately the same dimensions as the original pre-sintered piece.

These processes reduce to a minimum the necessary and costly diamond machining, normally required with hot and cold forming methods, and have worked well on a prototype basis. They may provide another way of manufacturing intricate ceramic shapes. A true net shape procedure has not yet been developed; however, this is a primary goal in manufacturing research.

Other hot forming techniques are based on similar methodology.

Coatings. Ceramic coating technologies include the traditional coatings, such as glazes, porcelain enamels, and slurry coatings, that were prized initially for their strength or resistance to chemical attack. Newer coating techniques provide

additional benefits derived from high purity thin layers, graded coatings, changes in surface structure, or thermal barrier protection. The newer processes include physical vapor deposition (PVD), chemical vapor deposition (CVD), flame and plasma spraying, and ion implantation. The method of application depends on both part composition and geometry. As in other hot forming processes, coatings are a final stage process.

Processes for ceramic coatings vary. A substrate, or piece to be coated, is generally prepared by one of a number of surface preparation techniques such as surface abrasion, chemical treatment, or a grading method to provide a strong bond between substrate and coating. Grading is a method of bonding the coating to the substrate with an intermediate layer, which is comprised of interconnected layers of both the coating material and the substrate. In some instances, the coating is applied and fired (for instance, slurry coatings); in others, such as PVD, a thin film is deposited in vacuum. CVD applies a coating by a chemical reaction at or above the surface to be coated. Flame and plasma spraying produce hot coatings which solidify after application.

Coatings can be applied to a wide range of materials to improve strength or corrosion/erosion resistance. Ceramic coatings are particularly useful when they combine the high performance properties of ceramics with the strength and ductility of metal. A number of ceramic materials can be used for coatings, including alumina, chromia, and zirconia. The major limitations in coating technology are attachment problems. Often, the ceramics coating

material will not 'wet' the substrate causing poor adhesion and insufficient bonding between the coating and substrate. New coating technologies need to be developed to apply coatings in many applications.

Ceramic Composites

Ceramic composites consist of two or more phases distinguished by crystal structure and/or composition. Ceramic composites have properties which are different from those of its individual constituents. Some ceramic-ceramic composites consist of ceramic fibers oriented within a ceramic matrix, ceramic fibers randomly oriented within a ceramic matrix, or dissimilar particles dispersed in a matrix with a controlled microstructure. Other two-phase ceramics with a boundary phase different from the host matrix are also considered composites. This latter group is used in ceramic dielectrics, capacitors, resistors, and other materials with piezoelectric or magnetic properties. The potential benefits of composites are a substantial increase in fracture toughness -- 2-5 times higher than conventional ceramics -- along with high strength and good thermal shock resistance.

Ceramic materials are brittle and crack initiation leads to rapid crack propagation and catastrophic failure. Particles dispersed within a matrix provide a means of slowing, deflecting, or stopping crack propagation. Thus, these ceramics dissipate crack energy and yield higher fracture toughnesses. Dispersion composites include titanium carbide (TiC) dispersed in alumina (Al_2O_3), used in

cutting tools, and transformation toughened zirconia. At the present time, structural ceramic composites are primarily in the experimental and early development stage.

Table 2.8 gives a general overview of the properties that can be achieved with fiber composites. Fiber composites consist of either aligned or unaligned fibers which are coated with the matrix material or simply pressed into a matrix. Processing techniques strongly influence the final properties. The matrix-fiber composite is either hot pressed or molded, and sintered to produce a high final density.

Incomplete fiber-matrix bonding is a problem in the fabrication of fiber composites. Pores may also congregate at the fiber-matrix interface, reducing the extent of composite fiber-matrix bonding. Figure 2.5 illustrates fibers within a matrix of various powder particle sizes. In this particular instance, the combination of large fibers with large particles leaves voids which create bonding problems.

The current cost of fibers is high (SiC fiber ~ $200/lb), as are the costs of processing techniques. Other fibers (Al_2O_3, for instance) have not shown as much promise for improved properties as have SiC fibers. The development of fiber composites is only in the early stages. Further development of new processing techniques for both fibers and composites shoulo produce a reduction in cost.

Table 2.8a. Strength and Toughness of Glass-Fiber Components*.[10]

	Fracture toughness ($MPa/m^{1/2}$)	Strength (MPa)	(1000 psi)
Glass-C or SiC fibers†	10–25	700	100
Glass-Al_2O_3 fibers‡		280	40
Glass matrix only§	1	70	10
Si_3N_4§	5	700	100

*Representative values at room temperature with ground surfaces. †See Ref. 16. ‡See Ref. 17. §Typical values presented for comparison with the composites.

Table 2.8b. Strength and Toughness of Glass-Fiber Composites Made by Co-pyrolysis*.[10]

	Fracture energy (WOF, J/m^2)	Strength (1000 psi)	(MPa)
Glassy carbon-graphite composite	700	30–50	210–350
Glassy carbon†	75	10–20	70–140
Graphite†	50	10–15	70–105
SiO_2 glass†	3		
Al_2O_3†	40		
Teakwood†	1500		

*Typical room-temperature values, Ref. 20. †Shown for comparison.

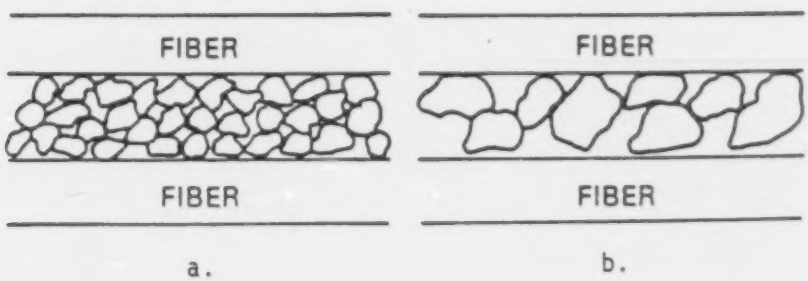


Figure 2.5. Schematic of processing fiber composites using powders to form the matrix. Two fibers with powder particles (small - a; larger - b) between them. Use of 10μm diameter fibers with powder particles a few micrometers in diameter can present problems.[10]

Summary

Although research into some areas of high-technology ceramics is still in the development stages, new non-traditional roles are being filled by ceramics. Current and near-term applications are summarized in Table 2.9. Examining a chart of typical ceramic properties with a comparison to those of various metals indicates a large range of possibilities for ceramic materials. The data in Table 2.4 and Table 2.10 indicate ceramic applications which overlap with those requiring strategic or imported materials such as chromium, cobalt, manganese, and platinum. A large potential for ceramic substitution does exist. However, some of the applications are not near-term: ceramic rotating parts for gas turbine applications are probably a medium- to long-term prospect.

The economic viability of using ceramics in many of the structural applications has not yet been demonstrated. Although the basic raw materials are plentiful and inexpensive, the procedures necessary to convert the raw material into a usable powder and a final part can be expensive. Mass production of many structural ceramics is not currently in operation. Studies show that while this is feasible, scaling up an experimental process to a manufacturing scale while retaining the desired properties and production reliability has not yet been achieved on a large scale.

Projections indicate that as new manufacturing technologies mature and the ability to design with brittle materials increases, prices will become competitive with existing technologies. This analysis includes the anticipated benefits from the increased

Table 2.9. Structural Applications for High Technology Ceramics.[5]

Near-Term

Wear Parts
Seals (high performance-scratch resistant)
Bearings (ball & roller)
Valves
Pads
Gates
Slides
Nozzles

Cutting Tools
Tips

Abrasives

Corrosion Resistant Parts
Piping
Valves
Seals
Gasifier Components (coal)
Coatings

Heat Engine Applications
Pushrods
Tappets
Seals
Glow Plug
Swirl Chamber
Turbocharger Rotors

Turbine Thermal Barrier Coatings
Braidable Shrouds

High Stiffness-to-Weight Structural Parts
Fiber Reinforced Spars
Tiles
Castings

By the Year 2000

Heat Exchanger Components
Metal Melting Furnaces
Glass Melting Furnaces
Coal Burning Furnaces
Incinerators

New Refractories

Heat Engine Applications
Diesel Combustion Zone
  Cylinders
  Piston Caps
Adiabatic Diesel
Turbine Static Parts
  Combustors
  Shrouds
Turbine Rotating Parts
  Missiles
Sensors and Probes

Gun Barrel Liners

Non-Engine Missile Parts
Radomes
IR Domes
Control Valves

Corrosion Resistant Parts
Synfuel Applications

Long-Term

Heat Engine Applications
Turbine Engine Rotating Parts
  Rotors
  Regenerators
  Military Aircraft
Stirling Engine Parts
Wankel Engine Parts
Aircraft APU

Solar Concentrator Targets

MHD Components

Fusion Reactor Components
First Wall Blanket

Table 2.10. Properties of Ceramics and Metals.[13]

Material / Property	Alumina	Cordierite		Mullite	Zirconia		Electrical Porcelain	Silicon Nitride			Sialon	Silicon Carbide			SUS 304	Nimonic 105	FC 25	AC 4C
		Low Density	High Density		Stabilized	PSZ		Pressureless Sintered	Hot Pressed	Reaction Bonded	Reaction Sintered	Pressureless Sintered	Hot Pressed	Self Bonded	(AISI 304)		(Gray Cast Iron SAE GJS00)	(SAE 356 (T)
Bulk Density	3.98	1.81	2.50	3.28	5.4	5.91	2.45	3.08	3.18	2.75	3.00	3.10	3.21	3.10	7.93	7.99	7.0	2.69
Open Porosity (%)	0	37	0	0	0	0	0	0	0	5	0	0	0	0	0	0	0	0
Flexural Strength RT (MPa) 1,000C (4 Point)	440 340	13 13	70 70	172 98	186 –	1020 400	157 –	650 470	845 680	298 300	355 355	500 475	930 820	530 530	765 (Tensile)	972 (Tensile)	240 (Tensile)	240 (Tensile)
Young's Modulus (GPa)	360	18	118	144	180	205	94	230	310	180	231	303	440	410	193	176-224	80-110	72
K_{IC} (MN/m$^{3/2}$)	4.5	–	–	–	11	8.4	1.8	5.3	5.8	3.6	2.2	2.4	4.4	4.8	(80-100)	(80-100)	(80-100)	–
Creep Resistance (MPa)	100 (1,000hr 1,200C)	–	–	60 (1,000hr 1,200C)	–	–	–	280 (1,000hr 1,000C)	–	250 (1,000hr 1,000C)	–	350 (1,000hr 1,000C)	–	–	70 (1,000hr 800C)	100 (100,000hr 800C)	–	165 (1,000hr 150C)
Linear Thermal Expansion Coefficient ($\times 10^{-6}$/C)	8.1	1.2	2.0	5.13	10.9	10.5	6.6-7.4	3.3	3.28	3.0	3.0	4.3	4.8	4.3	17.3	12.5	10-11	23.5
Thermal Conductivity (kcal/cm·sec·C)	0.07	0.003	0.010	0.018	0.005	0.007	0.004	0.070	0.048	0.048	–	0.14	0.19	0.18	0.039	0.028	0.12	0.38
Heat Capacity (cal/g·C)	0.2	0.12	0.17	0.15	0.18	0.12	0.28	0.19	0.17	0.19	–	0.20	0.20	0.20	0.12	0.11	0.13	0.23
Thermal Shock Resistance Parameter ($R = S\sigma/E\cdot\alpha$)	150	680	300	230	110	350	240	860	830	620	510	300	440	300	–	–	–	–
Oxidation Resistance (mg/cm^2)	–	–	–	–	–	–	–	0.1 (100hr 1,000C)	<0.1 (100hr 1,000C)	2 (100hr 1,000C)	–	<0.1 (100hr 1,000C)	1.5 (16hr 1,600C)	–	–	–	–	–
Melting Point (C)	2,030	1,440	1,450	1,810	2,600	2,600	1,100	1,900 (decomp.)	1,900 (decomp.)	1,900 (decomp.)	–	2,700 (decomp.)	2,700 (decomp.)	2,700 (decomp.)	1,400	–	1,150	555
Max. Use Temperature (C)	1,800	1,200	1,200	1,800	2,300	1,500	500	1,400	1,500	1,500	–	1,650	1,650	1,650	–	–	–	–

utilization of ceramics, including higher temperature use which will increase fuel efficiencies in engines. The reduction in weight due to the substitution of ceramics for metals in some parts will provide good strength-to-weight ratios, less rotating inertia, and a reduced reliance on strategic and critical materials. Better corrosion and erosion resistance will result in longer life and greater productivity. However, before these benefits can be realized, a number of technical, economic, and institutional barriers must be overcome.

References

1. Ceramics, Encyclopedia of Chemical Technology, Kirk-Othmer, 3rd ed., Vol. 5 (New York:John Wiley & Sons, 1979), p. 234.

2. Kingery, W.D., Bowen, H.K., and Uhlmann, D.R., Introduction to Ceramics, 2nd ed. (New York:John Wiley & Sons, 1976).

3. "U.S. Ceramic Market Data," American Ceramic Society Bulletin, Vol. 62, No. 5 (1983): 549.

4. Kenney, G.B. and Bowen, H.K., "High Tech Ceramics in Japan: Current and Future Markets," American Ceramic Society Bulletin, Vol. 62, No. 5 (1983): 590.

5. Johnson, L.R., Testia, A.P.S., and Hill, L.G., "A Structural Ceramics Research Program: A Preliminary Economic Analysis," Report ANL/CNSV-38, Center for Transportation Research, Argonne National Laboratory, March 1983.

6. "Fine Ceramics," Report, Fine Ceramics Office, Japan, Nov. 1982.

7. Norton, F.H., Elements of Ceramics, (Reading, MA:Addison-Wesley, 1974).

8. Witec California, Inc., Information Brochure, San Diego, CA, 1983.

9. Frados, J., ed., Plastics Engineering Handbook of the Society of the Plastics Industry Inc.," 4th ed. (New York:Van Nostrand Reinhold Co., 1976).

10. Rice, R.W., "Ceramic Composites - Processing Challenges," Reprint, Ceramic Engineering and Science Proceedings, Vol. 2, No. 7-8 (1981).

11. Didrichson, P., Dow Corning, Personal Communication (July, 1983).

12. Lawn, B.R., and Wilshaw, T.R., Fracture of Brittle Solids, (Cambridge, England:Cambridge University Press, 1975).

13. Kamo, R., "High Technology Ceramics for Japanese Heat Engines," Report Draft, Division of Policy Analysis, Advanced Technologies and Resources Policy Group, National Science Foundation, April 1983.

14. "New Materials Development Program (2)," Technocrat, Vol. 2, No. 2 (1982): 13-23.

3. COBALT

Introduction

With no domestic cobalt production of its own, the U.S. is dependent upon foreign sources for 93% of its requirements and obtains the remaining 7% from recycled scrap. More than half of current worldwide cobalt production is located in southern Africa which leaves the future supply and price of this critical commodity in some doubt. It was political instability in this part of the world in 1979 which caused an 8 fold increase in the price of cobalt from $5/lb to $40/lb. U.S. consumption of cobalt has since declined from 20 million pounds in 1979 to 11.7 million pounds in 1981, as illustrated in Table 3.1, due primarily to substitution and the worldwide economic recession.

The specific end uses of cobalt are illustrated in Table 3.2. In 1981, superalloys, primarily for industrial and aircraft gas turbine applications, accounted for 36% of cobalt demand; magnetic materials 14%; catalysts 11%, cutting and wear resistant materials 9%; and all other uses 30%. Ceramics are becoming increasingly attractive as substitutes for cobalt-bearing materials in many of these areas. For example, ceramics are a viable substitute for cobalt bearing metal parts in cutting tool, seal, nozzle, bearing, pump, pump lining, and other applications requiring good abrasion and wear resistance, low friction, and high temperature stability and strength. Ceramic ferrites also compete well with cobalt based permanent magnets. In general, ceramics could, overtime, eliminate

Table 3.1. Cobalt Use in the United States, %.[1]

		1979		1981	
Metallurgical	Superalloys	30		36	
	Magnetic materials	20	65%	14	69%
	Tool bits, dies, and others	15		19	
Non-Metallurgical	Catalysts	15		11	
	Driers	15	35%	12	8%
	Other	5		8	
		20 million pounds		11.7 million pounds	

Table 3.2. U.S. Consumption of Cobalt, by End Use.[1]

(Thousand pounds of contained cobalt)

End use	Quantity	
	1980	1981
Steel:		
Stainless and heat-resisting	47	35
Full-alloy	116	141
High-strength, low-alloy	W	W
Tool	321	170
Superalloys	6,285	4,195
Alloys (excludes alloy steels and superalloys):		
Cutting and wear-resistant materials[1]	1,344	1,076
Welding materials (structural and hard-facing)	620	488
Magnetic alloys	2,267	1,587
Nonferrous alloys	150	131
Other alloys	210	123
Mill products made from metal powder	W	W
Chemical and ceramic uses:		
Pigments	282	329
Catalysts	1,656	1,279
Ground coat frit	482	441
Glass decolorizer	40	40
Drier in paints or related usage	1,331	1,378
Feed or nutritive additive	75	58
Miscellaneous and unspecified	95	109
Total	15,321	11,580

W Withheld to avoid disclosing company proprietary data; included with "Miscellaneous and unspecified."
[1]Cemented and sintered carbides and cast carbide dies or parts.

up to 25% of current cobalt usage, assuming large increases in the price of cobalt and future research and development efforts in promising areas for substitution.

Superalloys

By far the most important and largest volume application of cobalt is as an alloying element. Its most critical alloying usage is in high temperature superalloys where it imparts wear and corrosion resistance plus strength. It is these excellent high temperature performance characteristics which renders cobalt strategically important to the aerospace industry and critically important to the petrochemical, stationary and vehicular gas turbine, and coal gasification industries.

Cobalt containing superalloys include cobalt-based (> 40% cobalt), and cobalt bearing nickel based (8-20% cobalt).[3] Cobalt-based alloys are used in the manufacture of gas turbine engines. Most of these alloys can be air-melted and air or argon remelted. They have good castability, good weldability, and good repairability. When carbide strengthed, cobalt-based superalloys exhibit good thermal stability, excellent thermal fatigue resistance, oxidation resistance, and hot corrosion resistance. These materials have an excellent high performance, high reliability record, as witnessed by their aircraft engine applications record. While high tech ceramic materials are potentially viable substitutes for superalloys, significant improvements in their reliability are required. This combined with the long and detailed approval process

perception of substitute ceramic materials for these applications, the projections of an average long-range 3% annual growth in cobalt consumption in these applications is realistic. However, various ceramic materials are viable substitutes for cobalt based cutting tool and other applications.

Cutting tools are generally developed for a specific function, and cemented carbide tools have found application in a wide range of machining operations, Table 3.3. Some of these applications have viable ceramic substitutes. Recent developments of Si_3N_4 cutting tools for cast iron machining provide productivity advantages and are cost competitive with WC-Co tools. As yet, Si_3N_4 tools are not in widespread use. In addition, aluminum oxide can be used either as a coating for cemented carbides, and as a monolithic tool bit material for cast iron and steel machining. Cermets, titanium nitride, and titanium carbide can also be used in some steel cutting applications. Superhard polycrystalline diamond, cubic boron nitride, and sialon are used in specialty cutting operations. However, no one material can be used in all cutting applications. There is substantial potential for ceramic substitution in this area as higher power, rigid machine tool technology is developed to accommodate ceramic cutting tools and consumer familiarity with these tool materials increases.

Other wear resistant applications of cobalt based materials are also being investigated for ceramic substitution. Ceramics have been used in seals, nozzles, and valves to replace Co-WC. Here again alternatives to cobalt-bonded cemented carbides find large

Table 3.3. Typical Application of Cobalt-Bonded Cemented Carbides.[3]

Straight Grade	Grain size	Application
97WC-3Co	Medium	Machining of cast iron, nonferrous metals and nonmetallic materials; excellent abrasion resistance and low shock resistance; the most wear resistant of the straight WC-Co grades; maintains a sharp cutting edge and makes long finishing cuts to close tolerance possible; also used for fine wire dies and small nozzles.
94WC-6Co	Fine	Machining nonferrous and high-temperature alloys.
94WC-6Co	Medium	General-purpose machining of work materials other than steel; also used for small and medium size compacting dies, coating dies, burnishing rings and nozzles.
94WC-6Co	Coarse	Machining of cast iron, nonferrous metals and nonmetallic materials; also used for small wire-drawing dies, compacting dies, small drawing dies and caps and rings. The hardest grade used in mining applications where impact is encountered, as in rotary percussive bits.
90WC-10Co	Fine	Machining steel and milling high-temperature metals (including titanium and its alloys) at low feeds and speeds; face mills, end mills, form tools, cutoff tools and screw-machine tools.
90WC-10Co	Coarse	Primarily used for mining roller bits and percussive drilling bits.
84WC-16Co	Fine	Primarily used for mining and metal-forming components.
84WC-16Co	Coarse	Metal-forming and mining components: medium and large dies where great toughness is required, blanking dies for punch presses, and large mandrels.
75WC-25Co	Medium	Metal-forming components for heavy impact applications, such as heading dies, cold extrusion dies, and punches and dies for blanking heavy stock.

required for aircraft engines implies that ceramic substitution in the application is a longer term prospect.

Cobalt bearing nickel-based superalloys account for the major alloying consumption of cobalt. Cobalt provides enhanced phase stability, workability oxidation and hot corrosion resistance, and generally improved mechanical properties to nickel based superalloys. Superalloys are sometimes ceramic coated when extended high temperature oxidation and corrosion resistance is required. This practice of ceramic coating superalloys has little effect on the overall usage of superalloy metal in these applications. However, it is those applications which are currently constrained by the performance limits of superalloys which are the primary focus of ceramic materials research efforts.

Cutting and Wear Resistance Materials

Cutting and wear resistant uses of cobalt include cemented, sintered, and cast carbides for cutting tool, die, and wear part applications. These components represented approximately 9% of the cobalt demand in 1981. Cobalt bonded cutting tools have replaced high speed steel tools in many cutting applications based on its superior wear resistance. Tungsten carbide cemented with cobalt has a higher fracture toughness than ceramic cutting tool materials. Co-WC also enjoys consumer acceptance in cutting tool and wear part applications. Significant progress has been made in recovery and recycling technology for Co-WC which gradually reduces the overall demand for cobalt. Without a change in consumer

applicability in particular components where higher corrosion, abrasion, and higher hardness are required. Ceramic substitutes can be designed for applications where a high fracture toughness is not a major requirement.

In Japan, a sintered form of Si_3N_4 is being developed to replace a high temperature cobalt alloy in a steel heat treatment furnace.[4] Experiments being carried out at the Keihin steel plant by Nippon Kikan and Asahi Glass indicate that the ceramic substitute eliminates the skid mark on a bloom without extra heat treating operations; significantly reduces thermal losses; reduces the refractory cost to less than half that of the cobalt alloy; and doubles the furnace life. The results of the skid-bottom furnace experiment demonstrate the performance advantages of using Si_3N_4 over a high temperature cobalt alloy. The ceramic substitute provides greater furnace yields, longer furnace life, and significant energy savings in fuel costs. It is also a 50% cheaper material than the cobalt alloy. As such benefits with ceramics continue to be demonstrated, expanded substitution for cobalt based components can be anticipated.

Magnets

The use of cobalt in magnets accounted for 14.4% of total consumption in 1981. Cobalt is used in permanent Alnico and Fe-Cr-Co deformable magnets (90%) and cobalt rare-earth magnets (10%). Demand for cobalt in magnets is price sensitive. With the high prices in the late 70's, substitution away from cobalt containing

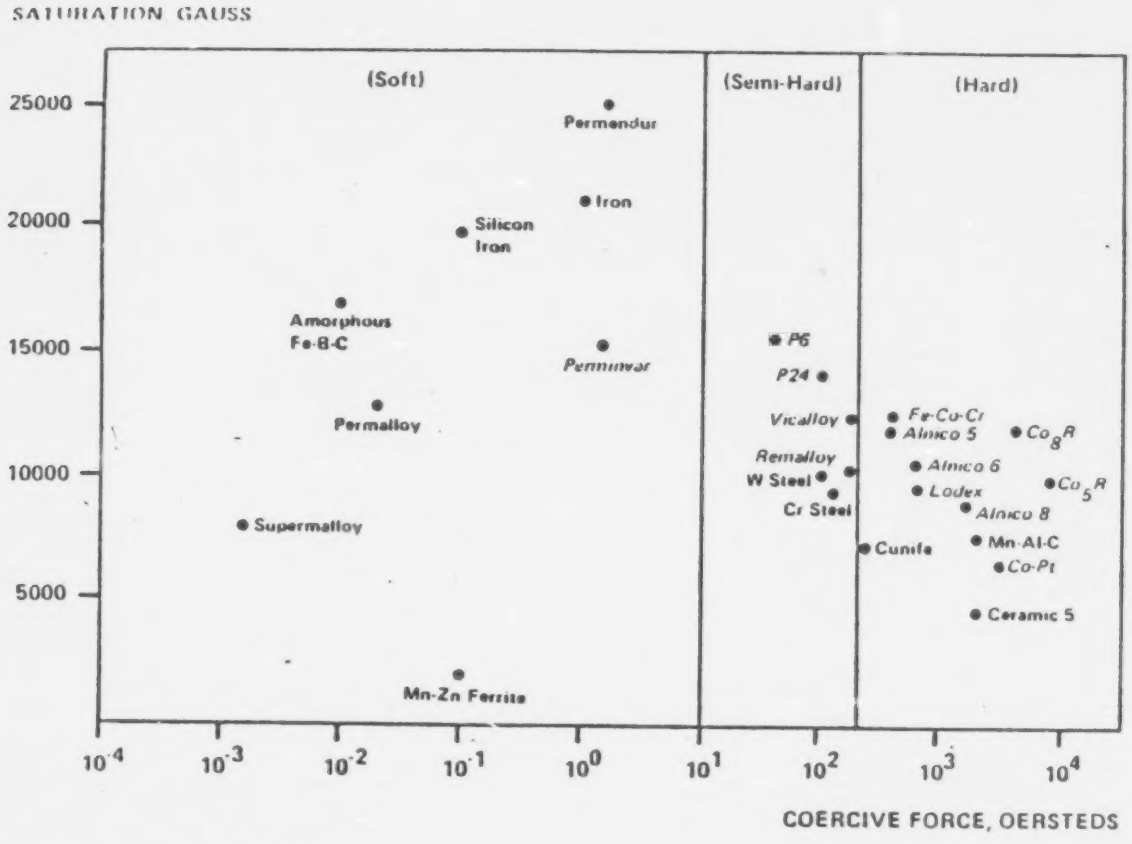
permanent magnets has been substantial.[3] In fact, cobalt use in magnets declined from roughly four million pounds in 1979 to 1.7 million pounds in 1981.

Magnetic properties are evaluated on the basis of the magnetic induction as a function of applied magnetic field. The saturation magnetization, Bs, and permanent flux density, Br, and coercive force, Hc, combined with maximum energy product (BHmax) determine the efficiency of the magnet. A classification of magnetic materials is provided in Figure 3.1. The properties of cobalt free permanent magnets are presented in Table 3.4. In comparing these properties with those of cobalt bearing magnets, Table 3.5, it is apparent that there are significant areas for substitution.

Some of these substitution possibilities have been implemented. Ceramic hard ferrites have penetrated 70% of the Alnico loudspeaker market due to the high price of cobalt. If cobalt prices remain constant, cobalt consumption in magnetic materials is projected to remain fairly constant. However, ceramics provide a low cost, magnetically efficient substitute that could potentially replace a greater portion of this market should cobalt prices increase significantly.

Catalysts

Catalysts represented 11.8% of domestic consumption in 1981.[2] and are used in a variety of applications including hydrotreating, hydroformulations, acid production, and pyrolysis gasoline hydrogenation. Catalysts are generally developed for specific



NOTE: Cobalt alloys are labeled in *italic type*.

SOURCE: Dr. D. L. Martin, "Possible Sustitutions for Cobalt-bearing Materials," Joint Intermag MMM Conference, New York, NY, July 19,1979.

Figure 3.1. Classification of magnetic materials.

Table 3.4. Cobalt-Free Permanent Magnet Materials.

Type	Composition Wt. percent	B_r (KG)	Hc (Oe)	$(BH)_{max}$ (MGOe)
Metallic				
Fe-Mo-Ni (A)	20Mo,5Ni,Bal. Fe	10.5	210	1.1
Fe-Mn	12Mn,Bal. Fe	15.0	85	1.1
Fe-Mn	16Mn,Bal. Fe	10.0	240	1.7
Alni	13Al,29Ni,Bal. Fe	6.6	600	1.4
Cunife (A)	60Cu,20Ni,Bal. Fe	5.5	530	1.4
ESD Fe (A)	72Pb,Bal. Fe	9.0	700	3.5
Mn-Al-Cu (A)	70Mn,29.5Al,0.5Cu	5.5	3000	7.5
Ferrite				
Ceramic 1	$MO.6Fe_2O_3$	2.3	1860	1.1
Ceramic 2 (A)	(for all where	2.9	2400	1.8
Ceramic 3 (A)	M equals one	3.3	2200	2.6
Ceramic 4 (A)	or more of	2.5	2300	1.5
Ceramic 5 (A)	Ba, Sr, Pb)	3.8	2400	3.4
Ceramic 6 (A)		3.2	2820	2.5
Ceramic 7 (A)		3.4	3250	2.8
Ceramic 8 (A)		3.9	2950	3.5
Ceramic (A)		4.2	2900	4.2

(A) Anisotropic.

Table 3.5. Cobalt-Containing Permanent Magnet Materials.

Type	Composition (Wt. pct. remainder Fe)	B_r (KG)	H_c (Oe)	$(BH)_{max}$ (MGOe)	$(BH)_m$ per unit Co	$(BH)_m$/Unit Co relative to Alnico 5
Alnico						
1	12Al, 21Ni, 5Co, 3Cu	7.2	470	1.1	28	1.2
2	10Al, 19Ni, 13Co, 3Cu	7.5	560	1.7	13	0.6
4	12Al, 27Ni, 5Co	5.6	720	1.4	28	1.2
5(A)	8Al, 14Ni, 24Co, 3Cu	12.5	640	5.5	23	1.0
5(A)(B)	8Al, 14Ni, 24Co, 3Cu	13.3	670	6.5	27	1.2
5(A)(C)	8Al, 14Ni, 24Co, 3Cu	13.5	745	7.6	32	1.4
8(A)	7Al, 15Ni, 35Co, 4Cu, 5Ti	8.2	1650	5.3	15	0.7
9(A)	7Al, 15Ni, 35Co, 4Cu, 5Ti	10.5	1500	9.0	26	1.1
-(A)(C)(D)	7Al, 14Ni, 40Co, 3Cu, 8Ti	9.7	1890	11.5	29	1.3
FeCrCo						
-	28Cr, 10.5Co	9.8	400	1.7	16	0.7
(A)(E)	33Cr, 7Co	11.9	485	3.3	47	2.0
(A)(E)	33Cr, 7Co, 2Cu	11.8	525	4.2	60	2.6
(A)	28Cr, 7Co	12.5	510	5.2	74	3.2
(A)(E)	33Cr, 23Co, 2Cu	13.0	1080	9.8	43	1.9
(A)(C)	24Cr, 15Co, 3Mo	15.4	840	9.5	63	2.7
RE-Co						
$SmCo_5$(A)	35Sm, 65Co	9.0	8500	20	31	1.3
$Sm(Co,Cu,Fe)_{7.5}$(A)	25.5Sm, 50Co, 8Cu, 1.5Zr	11.0	6400	30	60	2.6
Miscellaneous						
Vicalloy	10V, 52Co	8.8	300	1.0	2	0.1
Remalloy	17Mo, 12Co	10.5	250	1.1	9	0.4
E.S.D.32(A)	71Pb, 11Co	7.3	940	3.5	32	1.4
PtCo	77Pt, 23Co	6.5	4300	9.5	41	1.8

(A) Anisotropic, magnetic field treatment
(B) Directional grain
(C) Columnar
(D) High coercivity
(E) Deformation aging

applications. The ability to catalyze a reaction is closely tied to the materials electronic structure and the reaction desired. Although there are a number of ceramic catalysts, a significant cobalt price increase would be required to promote substitutions in this area.[5] Due to the nature of the industries utilizing co-catalysts it would be difficult to quantify the degree to which ceramics could substitute. It would also require large incentives (high cobalt price, or a new highly efficient catalyst) to cause substitution in this area.

Summary

The major uses of cobalt in superalloys, wear resistant materials, magnets and catalysts all have some potential for substitution which will reduce cobalt consumption. Chemical uses which comprise 25% of current cobalt demand are generally viewed as non substitutable. The recent high cost of cobalt provided a large driving force for substitution in many areas. Because of uncertain cobalt supplies and price, research efforts will continue in many fields to examine the possibilities for developing substitutes for cobalt. Much of this effort is focused on advanced ceramics.

REFERENCES

1. Coutsouradis, D., and Habraken, L., "Metallurgical Applications of Cobalt, A Critical Overview," Journal of Metals, Jan. 1983, Pg. 40.

2. Sibley, S.F., and Kirk, W.S., "Cobalt," Preprint for 1981 Minerals Yearbook, U.S. Bureau of Mines, U.S. Department of Interior, Washington, D.C.

3. "Cobalt Conservation through Technological Alternatives," National Materials Advisory Board, Commission on Engineering and Technical Systems, National Research Council, NMAB-406, National Academy Press, Washington, D.C., 1983.

4. "Translations on Fine Ceramics R&D Production Activities in Japan," Ceramics, Feb. 1983.

5. Satterfield, C.N., MIT Department of Chemical Engineering, Personal communication, June 1983.

4. CHROMIUM AND MANGANESE

Introduction

The Central Economy Countries and South Africa collectively produce 72% of the world supply of chromium and 60% of the world supply of manganese. The United States imports 91% of its chromium and 97% of its manganese requirements. The major use of both chromium and manganese is in the production of stainless steels (chromium) and general iron and steel production. These steels are used in a wide range of applications from aircraft and earthmoving machinery to automobiles. The expanding use of advanced ceramics will reduce the demand for these strategic materials by both direct and indirect replacement. For example, new ceramic based engine technology may reduce chromium requirements by direct substitution for such parts as valves. These ceramic engines may also eliminate the need for catalytic converters thereby indirectly eliminating the chromium requirement for this component. In addition, the use of ceramic coatings to enhance the wear, temperature, and chemical resistance of a specialty steel component directly reduces the quantity of substrate metal required. Clearly, the domestic demand for chromium could be somewhat reduced by advanced ceramics as these materials continue to evolve.

Chromium

In 1981, U.S. consumption of chromium included 57% metallurgical, 27% chemical, and 16% refractory applications.[1]

Chromium is used in a wide variety of products ranging from alloy, tool, stainless, and specialty steels to metal platings, leather tanning, textile dyes, and refractories. Projections of U.S. chromium consumption to the year 2000 by end-use sector are outlined in Table 4.1. Demand for chromium in the listed market sectors is expected to grow by an annual rate of roughly 3.2%, with the exception of refractories.[1] The reduction in the use of chromium based refractories is based on a projected decline in steel industry demand for these materials due to new process developments which require higher performance alumina, zirconia, and silicon carbide refractories.

Major deposits of U.S. chrome ore occur in Montana, Oregon, California, Washington, and Alaska. However, these deposits are not competitive with foreign sources due to their small size, low grade, and/or distance from consuming areas. The U.S. currently consumes roughly 550,000 short tons of chromium. Total domestic consumption of chromite ore and concentrates in 1981 was 879,000 tons which had an average Cr_2O_3 content of 38.3%. Recycling of stainless steel scrap accounts for roughly 9% of current chromium supply.

Applications

The specific end uses of chromium ferroalloys are illustrated in Table 4.2. The principal use of chromium is as an alloying element, the addition of which imparts corrosion and high temperature oxidation resistance to steels and nickel-based alloys. These high temperature properties are of critical importance to the

Table 4.1. Projections and Forecasts for U.S. Chromium Demand, by End Use (Thousand tons of Chromium).[1]

End use	1978 •	2000			
		Statistical projections. '	Contingency forecasts for United States		
			Forecast range		Probable
			Low	High	
Transportation	120	220	150	300	200
Construction	100	240*	200	310	280
Machinery	94	180	180	270	240
Fabricated metal products	44	87	50	110	90
Refractories	70	29*	20	60	30
Plating of metals	19	29	40	80	70
Chemicals	73	100*	110	160	120
Other	70	170	190	220	210
Total	590		940	1,510	1,240

• Estimated.

' Statistical projections, provided by the Branch of Economic Analysis, are derived from regression analysis based on historical time series data and forecasts of economic indicators such as GNP, FRB index. Projection equations with a coefficient of determination (R squared) less than 0.70 are indicated by an asterisk (*).

Table 4.2. U.S. Consumption of Chromium Ferroalloys and Metal in 1981, by End Use (Short tons, gross weight).[2]

End use	Low-carbon ferrochromium	High-carbon ferrochromium	Ferrochromium silicon	Other	Total
Steel					
Carbon	2,275	5,554	1,307	52	9,188
Stainless and heat-resisting	18,100	271,233	13,966	294	301,593
Full alloy	16,401	54,910	4,424	2,969	78,704
High-strength low-alloy and electric	2,611	4,151	2,307	2,545	11,614
Tool	558	3,927	125	--	4,610
Cast irons	948	8,978	198	512	10,634
Superalloys	3,718	3,085	W	2,478	9,281
Welding materials (structural and hard-facing)	737	805	--	164	1,706
Other alloys[1]	1,041	780	12	1,849	3,682
Miscellaneous and unspecified	2,014	328	144	23	2,529
Total	48,421	353,751	22,483	[3]10,886	433,541
Chromium content	30,769	207,122	8,258	7,199	253,348
Stocks, Dec. 31, 1981	6,194	46,601	1,801	[4]2,468	56,068

W Withheld to avoid disclosing company proprietary data; included with "Miscellaneous and unspecified."
[1]Includes magnetic and nonferrous alloys.
[3]Includes 3,835 tons of chromium metal.
[4]Includes 744 tons of chromium metal.

automotive, aerospace, petrochemical, nuclear, and power plant industries. Chromium also imparts hardenability, creep and impact strength, and resistance to wear and galling. Stainless steel represents 70% of domestic chromium ferroalloy consumption. There is currently no viable substitute for chromium in this application. Nickel, cobalt, columbium, vanadium, or molybdenum can be used to substitute for chromium in alloy steels. However, the low price and superior performance with chromium alloying make it the material of choice.

The areas in which ceramic technology could provide a reduction in the uses of chromium include high temperature superalloys, automotive applications, household appliances, plumbing fixtures, chemicals, and refractories.

The use of chromium ferroalloys and metal in high temperature superalloys, which are used primarily in gas turbine engines, is illustrated in Table 4.2. While turbine applications of superalloys are irreplaceable with present technology levels, further developments in silicon carbide and silicon nitride technology could qualify these high tech ceramic materials as viable substitutes. These ceramic materials can operate at higher turbine inlet gas temperatures and thereby provide either improved fuel efficiency or engine performance. Both monolithic ceramics and ceramic coatings have been proposed for these applications. SiC and Si_3N_4 use in gas turbines are presently only in the research stage, however if the technology develops this could replace up to 15,000-30,000 tons of chromium/year in this critical application.

The major applications of chromium in the average automobile are broken down by weight in Table 4.3. It is apparent that the single largest use of chromium in the automobile is in the catalytic converter, ~ 2 lbs in 1980. This 2 lb component represents approximately a third of the total chromium used in the automobile.[3] National Materials Advisory Board estimates have indicated that in an emergency the standard automotive engine could be built with only 0.39 lbs of chromium, plus the chromium required for the catalytic converter. Replacement of the standard engine with new ceramic engine technology could reduce chromium consumption by approximately 10,000 tons per year (see "Heat Engines" section). This estimate is based on the assumption that the new ceramic engine would not require a catalytic converter and that approximately 10 million cars per year would be produced.

Many household appliances and plumbing fixtures are made from stainless steels. These stainless steel components contain from 10 to 30% by weight chromium. In most of these applications enamel coatings could substitute for stainless steel. The enamels would coat lower chromium content steel or cast iron, and would provide a range of colors, corrosion and abrasion resistance, and easy cleansability at a low cost.

Substitution for chromium in chemical applications such as pigments and plating has also been successful. Cadmium yellow, organic yellow, and yellow iron oxide have been used as substitutes for chrome yellow in pigments. Nickel, cadmium, and zinc have been used to replace chromium in metal plating applications. These

bTable 4.3. Chromium Usage in U.S.-Built Passenger Cars Powered by Conventional Otto Cycle Piston Engines (pounds).[3]

	Actual Typical 1975 Full-Size Car (4,450 lb)	Estimated Average U.S. 1976 Car (3,750 lb)	Projected Average U.S. 1980 Car (3,000 lb)
Propulsion System			
Cylinder block, head, camshaft, valves	1.277	1.077	0.860
Cooling system	0.017	0.014	0.011
Electrical system	0.007	0.006	0.005
Carburetor, air intake, exhaust	0.118	0.099	0.079
Catalytic converter	3.335	2.587	2.070
Transmission (automatic)	0.169	0.142	0.114
Propulsion shaft, rear axle, differential	0.061	0.051	0.041
Subtotal	4.984	3.976	3.180
Chassis			
Deluxe wheel covers	1.440	1.214	0.971
Front suspension	0.250	0.211	0.169
Brakes	0.047	0.040	0.032
Steering gear	0.019	0.016	0.013
Steering wheel	0.028	0.024	0.019
Rear suspension	0.136	0.115	0.092
Lights	0.071	0.060	0.048
Miscellaneous	0.067	0.056	0.045
Subtotal	2.058	1.736	1,389
Body			
Windshield wipers	0.265	0.265	0.265
Seat belts	0.355	0.355	0.355
Windshield lower molding	0.276	0.069[a]	--
Roof drip moldings	0.203	0.171	0.137
Door window moldings	0.155	0.131	0.105
Chromium plate	0.060	0.051	0.041
Subtotal	1.314	1.042	0.903
Total chromium per car	8.356	6.754	5.472
Total without catalytic converter	5.766	4.764	3.402

[a] Used on an estimated 25 percent of total production.

substitutes are adequate in many but not all applications.

In the ceramic industry itself, chromium is used in a range of refractories, coatings, and as a constituent in glasses and glazes. The major use is in the refractories industry. These refractories are used in steelmaking and steel foundry processes. Table 4.4 indicates where chromium may be replaced by ceramic products. Most of the substitutes indicated in Table 4.4, have somewhat inferior properties to chrome bearing materials and are more expensive.

The major focus of ceramic research which could lead to the replacement of chromium has concentrated on new engine technology and coatings. The new engine technologies, because of their higher efficiencies, better fuel economy, potentially lower emissions benefits, have been in the forefront of research. Coatings are constantly being researched to improve corrosion and wear resistance, or to provide high temperature insulation to existing technology. Substitution has not been active in a number of areas due to the low cost and superior performance of chromium bearing materials.[4] Future use of ceramics as a substitute for chromium bearing alloys will occur only if chromium is unavailable or if significant increases in price occur. At the current level of chromium price and supply, and the general attitude of industry, little or no replacement of chromium by ceramics will occur.

Manganese

In 1981, domestic consumption of manganese was over 1 million tons. Of this million tons, 67.9% went into the production of

Table 4.4. Alternatives for Ceramic Products.[3]

Material	Application	Contained Cr_2O_3	Cr_2O_3 Demand, tons	Role of Cr_2O_3	Available Alternate Materials: Substitute Materials	Contained Cr_2O_3	Cr_2O_3 Savings, tons	Property Deficiencies	Required New Technology: Research Needed	Priority of Research	Probability of Research Success
Chrome and chrome magnesite brick	Furnace and kiln linings	18 to 23%	Ca 30,000	Improved slag resistance and thermophysical properties	Magnesite chrome brick	6 to 12%	20,000 to 24,000	Most applications significantly none, in copper converters less slag resistance	None	None	–
					Magnesite brick	0	30,000	Cost, lower slag resistance and volume stability	None	None	–
					Spinel	0	30,000	As above	Improved physicals	Low	Good
					Forsterite	0	30,000	As above	Improved physicals	Low	Good
					Dolomite	0	30,000	As above and hydration	Improved purity and physicals	Low	Good
Magnesite chrome brick	Furnace and kiln linings	5 to 16%	Ca 45,000	Slag resistance and thermophysical properties	Magnesite	0	45,000	Cost, slag resistance and volume stability	Establish minimum amount of Cr_2O_3 needed	Medium	Good

Table 4.4. Alternatives for Ceramic Products.[3](cont'd)

					Spinel	0	45,000	As above		
					Forsterite	0	45,000	As above		
					Dolomite	0	45,000	As above plus hydration		
Granular chrome-bearing materials	Furnace and kiln maintenance	18 to 44%	Ca 80,500	Thermal stability and slag resistance	Magnesite	0	86,500	Cost, volume stability	None	None
					Dolomite	0	86,500	Volume stability and hydration	None	None
					High Al_2O_3	0	40,000	Cost, availability, chemical compatibility	None	None
Granular chromite	Foundry facing sands	44+%	Ca 30,000	Chill, chemical and thermal stability	Zircon	0	30,000	Cost, availability, heat capacity and chemical resistance	None	None
					Olivine	0	30,000	Heat capacity and chemical resistance	None	None
					Quartz	0	30,000	Heat capacity, chemical resistance and thermal stability	None	None

manganese alloys and metals, 12.3% to pig iron and steel, 6.4% to dry cells and chemical uses, and 13.4% related miscellaneous uses.[5] The United States has no manganese mining industry. Manganese ore is imported from Gabon, Brazil, and South Africa, and is critical to the domestic steel industry.

The primary use of manganese is in the production of iron and steel.[6] There is no known substitute for manganese in the steelmaking process, and demand for manganese has been characterized as price inelastic. Substitutes for manganese will only come about through the replacement of manganese containing steels in specific applications. The only real potential for ceramic substitution being examined at the present time for manganese steels is the use of ceramics in heat engines. This, however, represents only a very small portion of total manganese consumption. Any other possibility is the use of ceramics based cells to replace dry cells which represent less that 2% of domestic manganese consumption.

The price for manganese has remained low which provides little incentive to substitute away from this metal. In general, the applications of manganese which require the metal are not seen as directly substitutable. Although replacements for steel in very specialized applications could become a reality, this would reduce manganese comsumption by an insignificant amount. The development of ceramic technology cannot be seen as a major replacement for this strategic metal.

References

1. Papp, J.F., "Chromium," Minerals Yearbook, Vol. 1, Metals and Minerals, U.S. Bureau of Mines, 1981.

2. "Morning, J.L., Matthews, N.S., and Peterson, E.C., "Chromium," Minerals Facts and Problems, U.S. Bureau of Mines, Bulletin 671, 1980.

3. "Contingency Plans for Chromium Utilization," National Materials Advisory Board, NMAB-335, National lAcademy of Sciences, Washington D.C., 1978.

4. M.R., McKinley, J.D., Steiner, B.W., and Bhansali, K.J., "Technical Aspects of Critical Materials Use by the Steel Industry", Volume I, Summary Report, U.S. Department of Commerce, NBSIR 83-2679-1, April 1983, Washington, D.C.

5. DeHuff, G.L., and Jones, T.S., "Manganese," Minerals Facts and Problems, U.S. Bureau of Mines, Bulletin 671, 1980.

6. Jones, T.S., "Manganese," Minerals Yearbook, Vol. 1, Metals and Minerals, U.S. Bureau of Mines, 1981.

5. PLATINUM

Introduction

In 1981, nearly 2 million troy ounces of platinum group metals were consumed in the United States, as summarized by industrial end-use sector in Table 5.1. Platinum, which represents 45% of this total, is used primarily as a catalyst as well as in electrical and corrosion-resistant applications (Figure 5.1). Roughly 51% of total domestic demand for platinum is generated by the automotive industry for use in catalytic converters. This single application of platinum has grown from practically zero in 1973 when automotive emission standards were mandated to nearly 450,000 troy ounces in 1981.

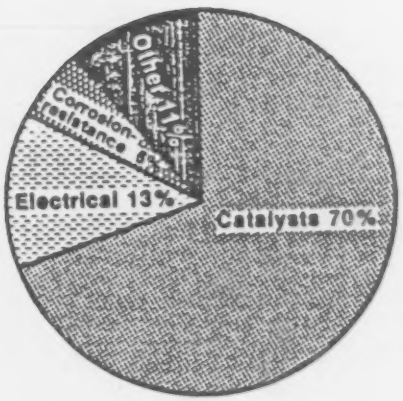
90% of the world's platinum supply is produced from deposits located within the USSR and South Africa. It is the near total dependence of the United States on these uncertain suppliers which motivates strategic planners to consider alternatives. U.S. platinum resouces are sizeable. However, these low-grade deposits cannot be economically mined at current platinum prices. Recently discovered platinum deposits in Stillwater Complex, Montana and Duluth, Minnesota may prove to be economically viable. The exact nature and size of these deposits is still under investigation. Taken together, the development of these reserves and the continued recycling of platinum used in non-sacrificial electrical and jewelry applications would certainly reduce, but certainly not eliminate, domestic dependence on foreign sources of platinum group metals.

Table 5.1. Platinum-Group Metals Sold to Consuming Industries in the United States.[1]

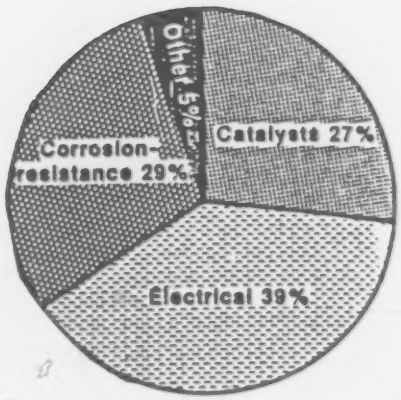
(Troy ounces)

Year and industry	Platinum	Palladium	Iridium	Osmium	Rhodium	Ruthenium	Total
1981:							
Automotive	448,677	129,214	83	--	30,009	1,300	607,283
Chemical	78,134	90,272	999	413	8,899	51,843	230,560
Dental and medical	18,759	255,114	173	250	35	238	274,544
Electrical	111,697	345,365	8,561	--	12,050	97,323	499,996
Glass	29,272	2,922	--	--	3,250	--	35,144
Jewelry and decorative	27,604	14,772	668	--	3,618	700	47,252
Petroleum	88,314	20,877	1,374	--	--	170	111,256
Miscellaneous	72,202	30,650	1,178	--	8,549	8,089	119,668
Total	872,639	889,186	8,416	663	62,110	97,658	1,920,672

[1]Comprises primary and nontoll-refined secondary metals.



Platinum
872,639 troy ounces



Palladium
889,186 troy ounces

Figure 5.1. Uses of platinum and palladium in 1981.[1]

It is the physical and chemical properties of platinum group metals, especially its chemical stability over a wide temperature range and highly catalytic nature, which make them attractive. It is these properties which uniquely qualify platinum for certain catalytic and high temperature process electrical applications. Interestingly, advances in the development and application of advanced ceramics may eliminate the need for, versus substitute for, platinum in automotive catalytic converter and some electrical applications.

Catalytic Applications

Catalysts are used in a variety of chemical reactions, usually requiring high temperature stability and specific electronic configurations. Platinum is by far the best catalyst for a number of applications. Its major use in automotive catalytic converters has doubled U.S. consumption over the last ten years. To date, research into other materials for catalytic converter usage have generated no substitute.[4] The current automotive converter consists of an Al_2O_3 ceramic housing with approximately 0.5 grams of a 70-30% mix of platinum palladium (Pt-Pd) coating the substrate. Other materials are either not sufficiently catalytic or are poisoned by the sulfur emissions. With the present internal combustion engine and further tightening of emission standards, it seems unlikely that there will be a direct substitution for Pt-Pd in this application. However, new adiabatic or high temperature engine technology may reduce or eliminate the need for a catalytic converter. These new

engine technologies, based on the use of both stationary and reciprocating ceramic components, include turbocharged and turbocompounded diesels, automotive gas turbines, and new engine designs such as the Stirling. For example, an adiabatic turbocompounded diesel engine fitted with advanced ceramic components may not require a catalytic converter due to the reduction in emissions expected at the higher operating temperature associated with this engine design. The gas turbine, which can use a variety of fuel types, is also expected to have much fewer emissions. This potential removal of the current automotive catalytic converter requirement would eliminate approximately 34% of PGM and 50% of the total demand for platinum usage in the United States. A discussion of the uses of ceramics in engine components will be presented later in the report.

Another large scale domestic catalytic usage of platinum includes petroleum hydrocracking and other chemical processing. These uses are not seen as currently being active platinum substitution areas for several reasons. Specifically, the actual cost of the catalyst is less than 1% of the total cost of many of these chemical processing techniques. Therefore, with a catalyst in use for a particular application, it is unlikely that a substitute will be installed unless there are significant advantages in terms of process efficiency. The chemical industry is generally conservative and is not inclined to risk an efficient large scale operation on a new, untried catalyst. Catalysts for these chemical

industry applications represent about 20% of domestic platinum usage.

Although many other catalysts exist, are in use, or under development (Co-based, Ni-based, and ceramic zeolites), none have been shown to work sufficiently well in specific chemical processes to warrant a direct substitution for those processes which erquire a platinum catalyst. However, research efforts to develop non-platinum based catalysts for applications which not utilize platinum are continuing. Some of the more interesting efforts include the potential development of oxide or ceramic catalysts. Proprietary industrial groups have ongoing research programs in this area. If successful, ceramic catalysts could substitute directly for the platinum equivalent in both automotive and chemical industry applications. One possibility for motivating active platinum substitution would be if platinum prices increase more than ten fold. It might then prove economical to use other catalysts in chemical applications which, though less efficient, could prove successful in some operations.

Another possiblity for platinum substitution is the development of metglas (metallic glass) alloys which, with high surface concentrations of phosphours, have indicated catalytic characteristics potentially compatible with chemical industry applications. The development of this new class of catalytic material is currently under development and analysis by several large domestic firms including Exxon and DuPont.[6]

Electrical Applications

Electrical uses for platinum and palladium account for 13% and 39% of consumption, respectively. These uses include relays, voltage regulators, meters, thermostats, thermocouples, heating elements, and some wiring. One of the major uses of platinum group metals is in telephone switching equipment as relay contacts. These components are either pure Pd or 60%Pd-40%Ag, both of which exhibit low arc erosion and wear. Part of the platinum heating element market has already been replaced by other types of heating elements such as graphite, SiC, Mo, $MoSi_2$, and other refractory metals. These materials are generally less expensive than platinum group metals and can be used in the same temperature ranges. However, platinum is still used in experimental furnaces because of its stability and chemical inertness at high temperatures.

The new computers currently being developed require advanced ceramic chip carriers and packages which will allow faster signal response and more complex electrical interconnections. High melting point molybdenum, tungsten, and platinum conducting wires are currently used to maintain the integrity of the circuit driving the very high temperature firing cycles required by the ceramic components. The use of copper and gold connections would increase the electrical conductivity by a factor of five to seven. Just such a substitution may be possible as new powder processing and component fabrication techniques are developed for advanced ceramics. Recent research with barium titanate ($BaTiO_3$) has indicated that, with appropriate processing control, this ceramic

demonstrates adequate electrical properties and can be densified at low firing temperatures. Consequently, the use of $BaTiO_3$ would facilitate the use of less expensive and less critical materials in advanced microcircuitry. Continuing advances in the processing of advanced ceramics indicate that low temperature firing may be possible with other ceramic materials, thereby expanding the potential for removing high temperature conductors from microcircuitry.

Other Applications

Very few of the other uses for platinum seem to have any direct ceramic substitutes. Platinum stirrers and liners are seen as critical to glass making processes. Dental and medical uses require platinum for its strength, color (teeth), and corrosion resistance. Jewelry and decorative use can of course be eliminated in times of crisis, but remain a stable part of the consumer market for platinum.

Summary

The potential substitution or elimination of platinum usage may be accomplished indirectly, and potentially directly, through the use of advanced ceramics. In the case of automotive catalytic converters, the use of advanced ceramics in hot, combustion zone, engine components may eliminate the need for subsequent emission control. Alternatively, if successfully developed, ceramic catalysts may substitute directly for platinum based systems. In

the electronic area, it is new ceramics with low firing temperature requirements which eliminate the need for critical electrical conductors capable of enduring initial, high temperature, ceramic processing steps. Emerging advanced ceramics clearly represent an opportunity to modify many existing automotive and electrical applications of platinum group metals.

References

1. "Platinum," Bureau of Mines Minerals Yearbook, 1981.

2. "Platinum," Minerals Facts and Problems, U.S. Dept. of Interior, 1980.

3. "Supply and Use Patterns for the Platinum-Group Metals," National Materials Advisory Board, NMAB-359, 1980.

4. Satterfield, C.N., "Department of Chemical Engineering, MIT, Personal communication.

5. Bryzik, W., and Kamo, R., "TACOM/Cummins Adiabatic Engine Program," SAE 830314, Warrendale, PA, 1982.

6. Allied Corporation, Personal communication.

6. HEAT ENGINES

Advanced ceramic components considered for use in heat engine applications, including diesel, gas turbine, and other proposed engine technologies, would replace specialty steels and superalloys containing chromium, cobalt, and small amounts of manganese in such hot zone components as turbochargers, valves, and valve seats. The major impact on critical materials would be the elimination of the catalytic converter. Catalytic converters account for approximately 50% of domestic platinum consumption, 34% of platinum group metal consumption and 33% of the chromium (2 lb/car) used in a standard automobile.[1]

Both direct and indirect fuel savings could be achieved through the use of ceramic components in heat engines. The thermal efficiencies associated with the higher operating temperatures directly result in energy savings in gas turbines. Similarly, higher thermal efficiencies and turbocharging/turbocompounding in diesel engines result in direct energy savings of 10% and 15%, respectively.[4] Indirect energy savings result from the elimination of engine cooling requirements and potentially lubrication, thereby reducing parasitic losses of engine power. Similar energy savings could be derived from turbocharging the standard internal combustion automobile engine. The improvement in overall efficiency and performance and potential reductions in engine cost provide the major driving force for this substitution. Additional benefits may be derived by ceramic substitution for critical materials. An

analysis of the current state of high tech ceramic materials development for the diesel and gas turbine engine follows.

Government Programs

Government programs for heat engine development began as early as 1940 and focused on the development of monolithic ceramic blades for gas turbine applications. However, even with the potential energy conservation and performance benefits promised by ceramics in this application, initial results were discouraging and the programs were terminated. A change to cermet blades (ceramic/metal composites) was made in the 1950's. It was hoped that these composites would combine the best properties of the ceramic with the ductility of the metal. However, this attempt to develop cermet turbine hot section engine components was also unsuccessful. These cermet programs were also discontinued, and it was not until the early 1970's that research to reconsider the possibility of using ceramics in heat engines was renewed. Figure 6.1 provides a general overview of these ceramic engine development programs. A short summary of some of the major programs follows.[2]

In 1971, the Defense Advanced Research Projects Agency (DARPA) initiated a program at Ford Motor Company to develop ceramics for small turbine engines. The program included engine design with brittle materials, materials development, manufacturing and process development, and engine and component feasibility demonstrations. The program focused on a 200 hp automotive gas turbine (AGT) with a required life cycle of 175 hours at 1050°F and 25 hours at 1375°C

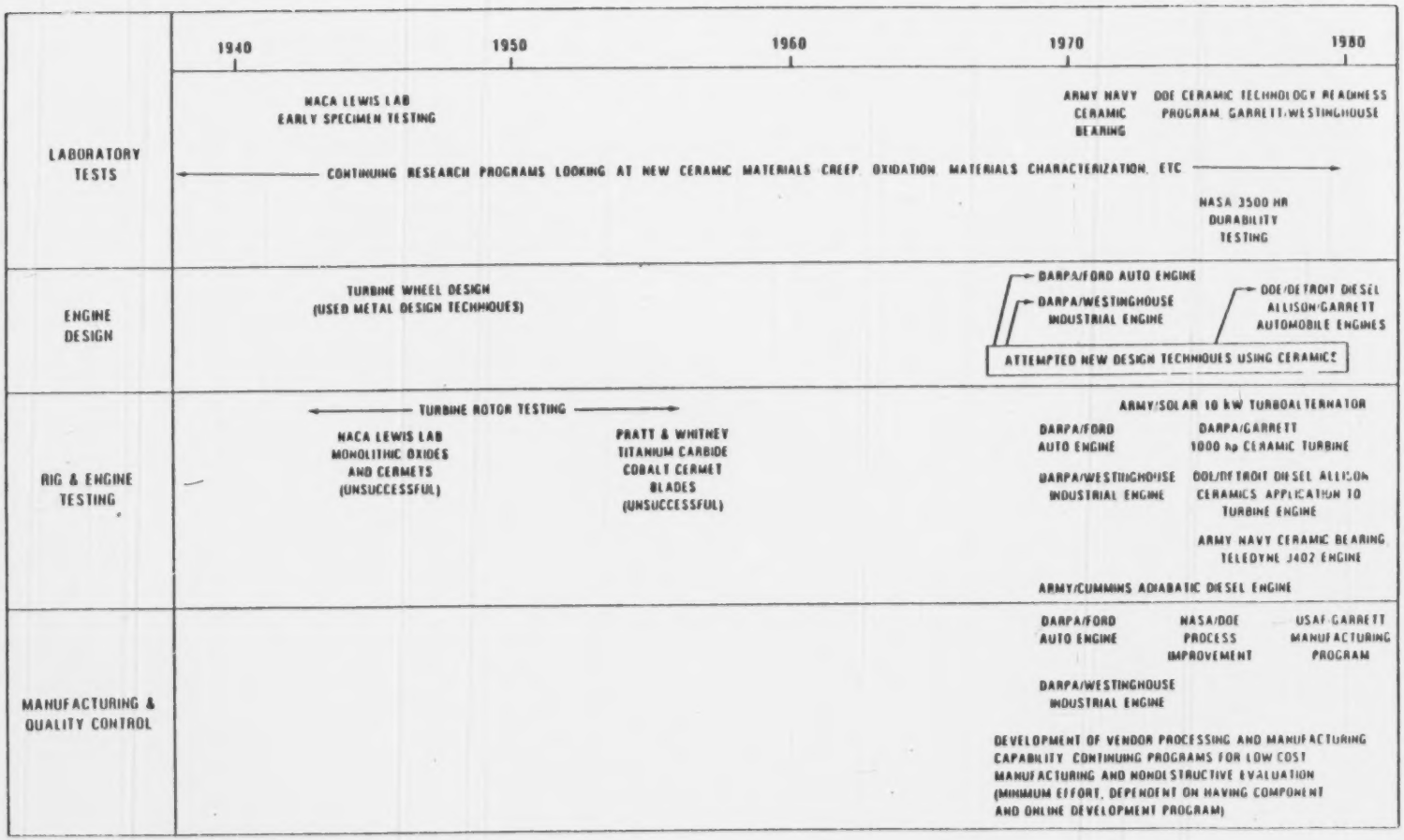

1940
1950
1960
1970
1980
LABORATORY TESTS
NACA LEWIS LAB EARLY SPECIMEN TESTING
ARMY NAVY CERAMIC BEARING
DOE CERAMIC TECHNOLOGY READINESS PROGRAM GARRETT/WESTINGHOUSE
CONTINUING RESEARCH PROGRAMS LOOKING AT NEW CERAMIC MATERIALS CREEP OXIDATION MATERIALS CHARACTERIZATION, ETC
NASA 3500 HR DURABILITY TESTING
ENGINE DESIGN
TURBINE WHEEL DESIGN (USED METAL DESIGN TECHNIQUES)
DARPA/FORD AUTO ENGINE
DARPA/WESTINGHOUSE INDUSTRIAL ENGINE
DOE/DETROIT DIESEL ALLISON/GARRETT AUTOMOBILE ENGINES
ATTEMPTED NEW DESIGN TECHNIQUES USING CERAMICS
RIG & ENGINE TESTING
TURBINE ROTOR TESTING
NACA LEWIS LAB MONOLITHIC OXIDES AND CERMETS (UNSUCCESSFUL)
PRATT & WHITNEY TITANIUM CARBIDE COBALT CERMET BLADES (UNSUCCESSFUL)
ARMY/SOLAR 10 kW TURBOALTERNATOR
DARPA/FORD AUTO ENGINE
DARPA/GARRETT 1000 hp CERAMIC TURBINE
DARPA/WESTINGHOUSE INDUSTRIAL ENGINE
DOE/DETROIT DIESEL ALLISON CERAMICS APPLICATION TO TURBINE ENGINE
ARMY NAVY CERAMIC BEARING TELEDYNE J402 ENGINE
ARMY/CUMMINS ADIABATIC DIESEL ENGINE
MANUFACTURING & QUALITY CONTROL
DARPA/FORD AUTO ENGINE
NASA/DOE PROCESS IMPROVEMENT
USAF GARRETT MANUFACTURING PROGRAM
DARPA/WESTINGHOUSE INDUSTRIAL ENGINE
DEVELOPMENT OF VENDOR PROCESSING AND MANUFACTURING CAPABILITY CONTINUING PROGRAMS FOR LOW COST MANUFACTURING AND NONDESTRUCTIVE EVALUATION (MINIMUM EFFORT, DEPENDENT ON HAVING COMPONENT AND ONLINE DEVELOPMENT PROGRAM)

Figure 6.1. General history of ceramic programs for engines [2]

turbine inlet temperature. Another DARPA sponsored program was carried out at Westinghouse Electric Company. This program's goal was to develop large ceramic vanes for a 30 MW utility gas turbine, but it stalled at the stationary test rig stage. The costs of the rotating test equipment were high and the prohibitively long development time severely constrained this program. Neither of these programs were successful in demonstrating the actual engine feasibility of ceramic components, because they never progressed past the initial testing stage.

In 1972, a joint Army/Navy in-house program was set up to develop ceramics for bearing applications. The program focused on the turbine engine mainshaft roller bearing, using ceramics as the rollers. The processing technology for ceramic bearings has developed significantly, but they still are not economical for any but military use. Ceramics are being used in specialized military application where low wear, low friction and high temperature and corrosion resistance are required.

The Army, in conjunction with Solar Turbine Company, has been examining ceramics for use in accessory power units (APUs) and ground generator sets. Ceramics were proposed for nozzle guide vanes to help reduce the erosion caused by sand and dust in small (10MW) gas turbines. Ceramic vanes and shrouds have operated successfully for more than 250 hours in these turbines. The successes of this program are listed in Table 6.1. Further work is ongoing to reduce ceramic fabrication costs.

Table 6.1. Meradcom - Solar 10kW Program Highlights.[23]

- 250 hour engine performance run with HPSN vanes and RS-SiC shrouds - successful
- 1000 hour rig test of HPSN roller bearing - successful
- Manufacturing technology program aimed at affordable vanes is ongoing

The Army is also funding a joint program with Cummins Engine Company to develop an adiabatic diesel engine with greater payload, greater erosion resistance, and the ability to use different fuels. The adiabatic diesel could also reduce maintenance requirements and have a greater battlefield survivability.[2] Ceramic parts for a 400 hp diesel truck engine include piston caps and cylinder liners. All components are tested in a single cylinder test rig before engine installation. The advantages of the ceramics are increased fuel efficiencies through higher temperature operation and elimination of the cooling system. This program has been somewhat successful, and Figure 6.2 illustrates the potential spin-off from the military applications to civilian markets.

The current DARPA program for ceramic gas turbine demonstration was initiated in 1976. State of the art ceramic materials were used in a 715 Nb Garrett turboshaft engine. Turbine inlet temperatures averaged about 1200°C and peak temperatures reached 1375°C. The program was specifically aimed at materials characterization. Final results indicated that the static ceramic parts were less reliable than the rotating parts.

The Department of Energy (DOE) began two programs in the mid 1970's to develop an automotive gas turbine (AGT) by 1985 which would have 30% greater fuel economy than existing engines. The first program, referred to as AGT 100, is with Detroit Diesel Allison (DDA), a division of General Motors Corporation, and included the development of materials and processes, manufacturing technology, non-destructive testing techniques, engine design, and a demonstration of part reproducibility.

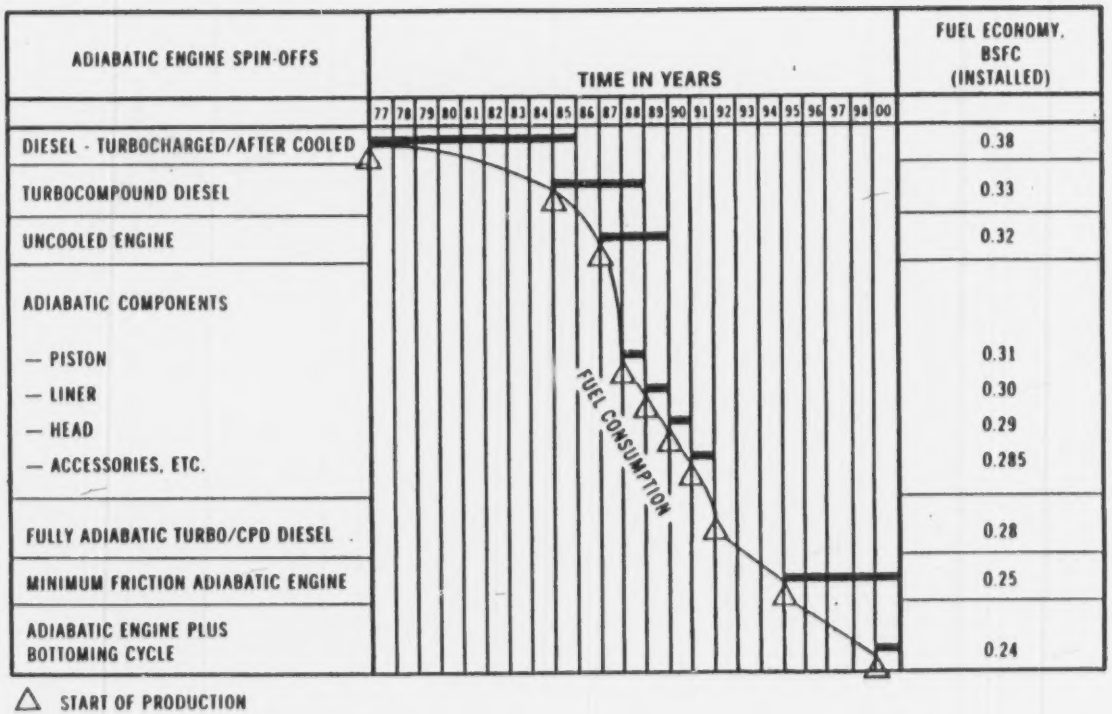


Figure 6.2. Predicted production date adiabatic engine spin-offs engine programs.[2]

The second, parallel program with Garrett and Ford, referred to as AGT 101, is developing a 100 hp automotive turbine with a maximum turbine inlet temperature of 1375°C. This engine will have a ceramic combustor, gasifier, turbine, and regenerator. Testing of all ceramic parts except the turbine rotor is underway, and tests of an all ceramic engine will take place in 1984.

In the mid-1970's DOE initiated a separate technology readiness development program, a portion of which examined the use of ceramics for large utility gas turbines using coal derived fuels. The first phase of the program created a baseline design for ceramic turbines, materials screening for erosion/corrosion, and the preparation of a technology plan. This program was terminated with no plans for continuation.

A thorough materials screening and evaluation of ceramic turbine materials, sponsored by the U.S. Air Force Wright Aeronautical Laboratories, is ongoing at the Illinois Institute of Technology (IIT).[3] The program has been used to develop materials specifications or criteria for ceramics in turbines. Evaluation of materials for different parts and from different manufacturers has been included.

All of these programs have enjoyed some level of success. They have demonstrated the feasibility of ceramic components and have delineated the technological developments necessary in order for ceramics to be viable components in heat engines. One major problem has been the need to develop non-destructive evaluation techniques, since present techniques are not adequate for large-

scale production. The use of ceramics in gas turbines still requires further research and development. The early applications will be in diesel engines, piston parts, and turbochargers with future potential focusing on gas turbines. No plans currently exist for use in commercial turbine engines.

Diesels

The high temperature insulating properties of ceramics make them attractive for use in diesel engines. The basic diesel engine loses 28% of its power through cooling and 36% to exhaust gases (Figure 6.3). Ceramics can reduce this cooling loss by more than 10%, and heat recovery could reduce exhaust gas losses. This increase in thermal efficiency, corresponding to an increase in overall engine performance, provides a large incentive for engine designers and manufacturers to incorporate ceramics into a new "adiabatic" diesel.[4] A truly adiabatic engine loses no heat in the engine cycle, an event impossible with any technology. However the uncooled engine concept possible with ceramic components leads to a greatly enhanced thermal efficiency. The feasibility of using ceramic components and/or coatings has been demonstrated on a 250-500 hp range diesel engine. At the present time, these diesels are being developed for military applications, but the technology, once developed, can be transferred to commercial vehicles.

The desired material characteristics of adiabatic engine components and their possible ceramic substitutes are listed in Table 6.2. These possible substitutes include zirconia, silicon

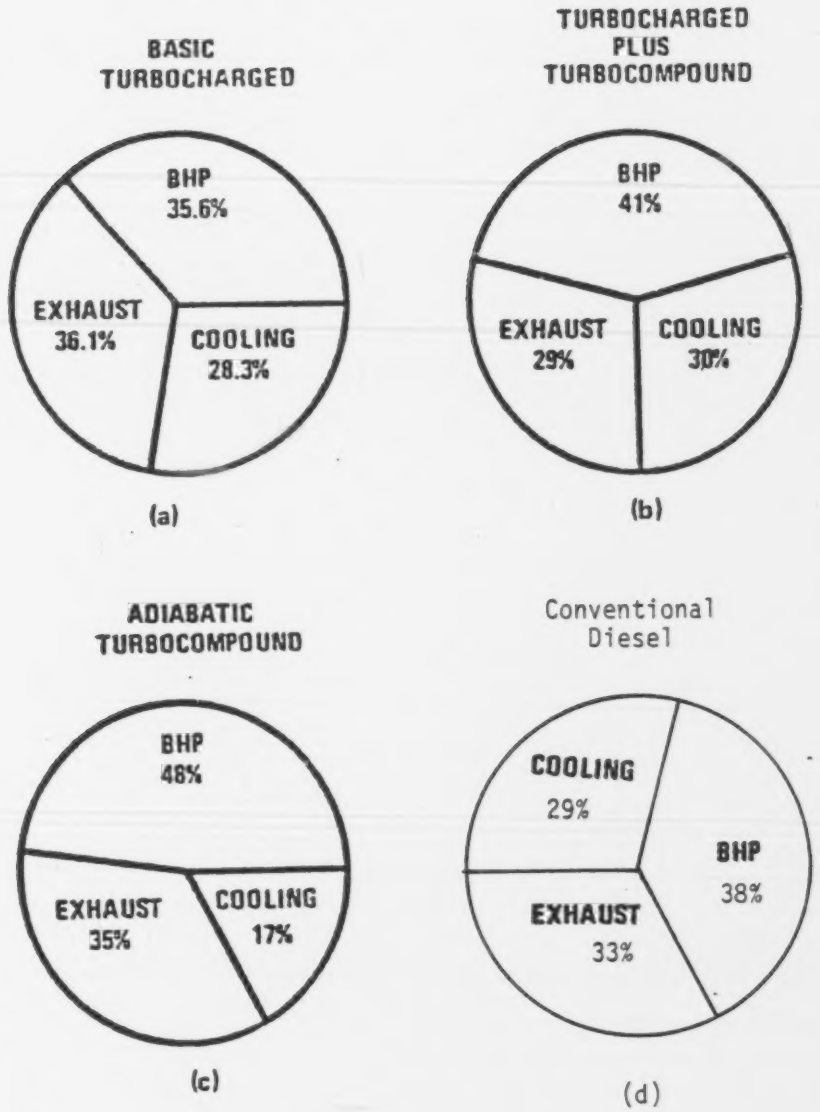


Figure 6.3. Energy balance comparison (diesel engine).[4]

Table 6.2. Summary of High Technology Ceramic Components for Adiabatic Engines in Japan and U.S.A.[5]

ADIABATIC COMPONENTS	DESIRED CHARACTERISTICS: LOW FRICTION	LIGHT WEIGHT	INSULATION	WEAR RESISTANCE	HEAT RESISTANCE	CORROSION RESISTANCE	EXPANSION COEFFICIENT	HIGH TECHNOLOGY CERAMICS	U.S.A.	JAPAN
PISTON		●	●		●	●	●	Si_3N_4, PSZ, TTA	PSZ/Coating	SSN
PISTON RING				●	●			SSN, PSZ, COATING	Plasma Coating	METAL
CYLINDER LINER	●			●	●	●	●	Si_3N_4, PSZ, COATING	Cr_2O_3	SSN
PRECHAMBER			●		●	●		PSZ, Si_3N4	NONE	NONE
VALVE		●	●	●	●	●		SSN, PSZ, COMPOSITE	Insulated Metal	METAL
VALVE SEAT INSERT			●	●	●	●		PSZ, SSN	PSZ	SSN
VALVE GUIDES	●		●		●	●		PSZ, SSN, SiC	PSZ	NONE
EXHAUST / INTAKE PORTS			●		●	●		ZrO_2, Si_3N_4, $TiO_2Al_2O_3$	TIALET	METAL
MANIFOLDS			●		●	●		ZrO_2, Si_3N_4, $TiO_2Al_2O_3$	Z_rO_2	METAL
TAPPETS		●		●		●		PSZ, SiC, Si_3N_4	METAL	SSN
MECHANICAL SEALS	●			●		●		SiC, Si_3N_4, PSZ	SiC	SSN
TURBOCHARGER										NONE
TURBINE ROTOR		●	●		●	●	●	Si_3N_4, SiC	SSN	--
TURBINE HOUSING			●		●	●	●	LAS	METAL	--
HEAT SHIELD			●		●	●	●	Z_rO_2, LAS	Z_rO_2	--
CERAMIC BEARINGS	●	●		●	●	●	●	SSN	HIDSN	--

NOMENCLATURE :
SSN - SINTERED SILICON NITRIDE
PSZ - PARTIALLY STABILIZED ZIRCONIA
LAS - LITHIUM ALUMINA SILICATE
TTA - TRANSFORMATION TOUGHENED ALUMINA

nitride, tialet ($TiAl_2O_5$), silicon carbide, and lithium aluminium silicate. Ceramic materials are being considered for use as monolithics (cast as a single unit), coatings, and composites. A cross section of a proposed adiabatic engine design complete with ceramic components is presented in Figure 6.4.

The required material properties for the adiabatic diesel engine are in Table 6.3. The materials chosen for hot section components should withstand temperatures above 198°C, have relatively good fracture toughness, high strength, be insulating in nature, and be resistant to thermal shock. In order to be compatible with the cast iron engine block, materials should have a high thermal expansion coefficient. Ranking these material requirements in order of importance is not a straightforward task. The insulating properties of the material are important, but without high temperature strength and reasonable toughness, a material would not be suitable for the engine environment.

Partially stabilized zirconia (PSZ) is thought to meet many of the requirements for diesel components, including piston, piston ring, cylinder liner, valve parts, tappets and mechanical seals. The wide variation in the properties of commercially available zirconias are listed in Table 6.4. These properties vary widely and depend strongly on the manufacturer, dopant, initial powders, and processing technique. Strengths vary from 200-900 MPa and toughnesses from approximately 3-15 $N/m^{3/2}$. Piston caps and cylinder liners have been fabricated by slip casting a ceramic part or by plasma spraying coating to the metal component, providing a

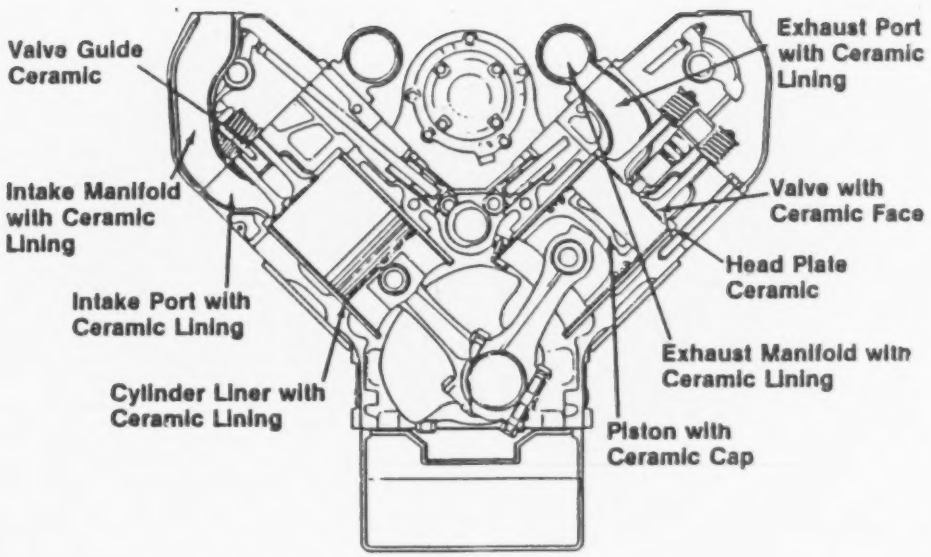

Valve Guide Ceramic
Exhaust Port with Ceramic Lining
Intake Manifold with Ceramic Lining
Valve with Ceramic Face
Head Plate Ceramic
Intake Port with Ceramic Lining
Exhaust Manifold with Ceramic Lining
Cylinder Liner with Ceramic Lining
Piston with Ceramic Cap

Figure 6.4. Cross section end view of 750 Hp diesel engine.[4]

Table 6.3. Typical Desired Material Properties for an Adiabatic Type Diesel Engine.[5]

Temperature Limit , ^{o}F		>1800
Fracture Toughness, K_{IC}		> 8.0
Flexural Strength, MPa	@ R.T.	> 800
Thermal Conductivity, K		< 0.01
Thermal Shock Resistance,	$\Delta T\ ^{o}C$	> 500
Coefficient of Expansion x $10^{-6}/\ ^{o}C$		> 10

Table 6.4. Mechanical Property Comparison
Polycrystalline PSZ.[5]

Material	ρ (g/cm^3)	H (GPa)	σ (MPa)	K_{IC} ($MPa\text{-}m^{1/2}$)	γ_f (J/m_2)	E (GPa)	ν	ΔT_c (°C)	Microstructure and XRD Phase Analysis
A. JAPAN (Y_2O_3)	5.75	11.7	900	4.7	50	201	0.32	375	0.1 - 0.5 μm 2-10μm duplex, cubic, tetrag. same monoclinic
B. AUSTRALIA (MgO)	5.75	9.4	700	>8-15	>160	200	0.24	425	10.40 m, 0.1-0.3 μm precipitates; cubic, tetrag., monoclinic
C. GERMANY (Y_2O_3)	5.77	11.6	650	>7 - 8 ~15	>120 >500	209	0.31	325	similar to "B".
D. U.S.A. (Y_2O_3)	5.24	11.0	200	2.7 - 2.9	21.25	170	0.29	-	5-20 μm, no precipitates cubic ?
E. U.S.A. (M_2O)	5.08	10.3	300	6.0 - 6.1	111 - 115	162	0.27	350	1-10 μm, 0.1 μm precipitates monoclinic, cubic and tetragonal
F. U.S.A. (M_2O)	-	9.2 ~11.5	430	4.7	60	192	0.30	225	55 μm, precipitates 0.1 - 0.3 μm

high-temperature material to interface with the combustion products. Examining thermal expansion coefficients of typical ceramics (Figure 6.5) indicates that zirconia has the value closest to cast iron and other metals. Zirconia also has a low thermal conductivity (Figure 6.6); therefore it is the best choice for insulating the combustion chamber. At the present time, plasma sprayed zirconia coatings have proved most effective in these applications, although the design for cylinder liners will require coatings approximately 2 mm thick which are not yet feasible. The coating has a lower thermal conductivity than the monolithic PSZ ceramic and does not require expensive finishing operations. It is not as impermeable or as thermal shock-resistant; however, the coated metal part has higher strength and toughness than the current monolithic ceramic part. As the technology evolves, monolithic components are scheduled to be incorporated into the engine.

The high thermal expansion coefficient (Figure 6.5) facilitates ceramic/metal joining. A shrink-fit monolithic ceramic cylinder liner used in the combustion chamber, places the ceramic in compression, thus maximizing its strength. Stress of up to 35,000 psi have been calculated for peak temperatures of approximately 1100°C for the web of a cylinder head hot plate. Therefore, PSZ, which does not have good high temperature strength, must withstand this level of stress in order for a monolithic cylinder liner to be a viable application.

Ceramic materials in general, and PSZ in particular, would reduce the overall weight of the engine and eliminate the use of

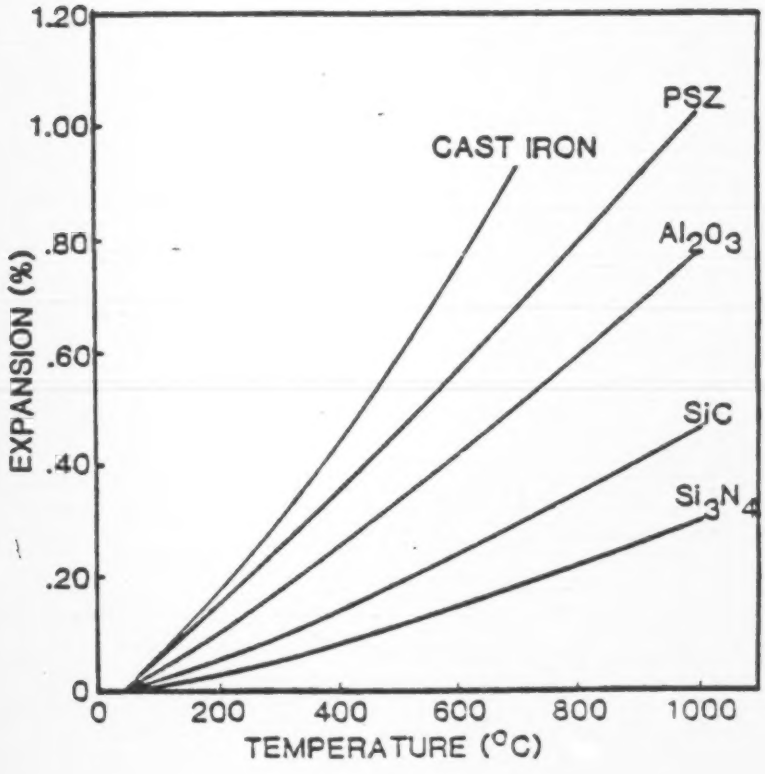


Figure 6.5. Thermal expansion of typical ceramics and cast iron.[4]

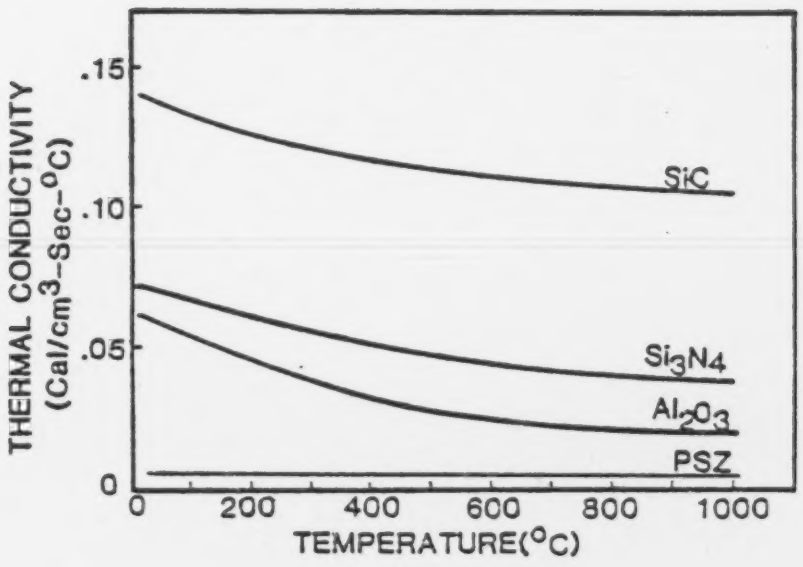


Figure 6.6. Thermal conductivities of typical ceramics.[4]

high temperature metals. However, zirconia may not be the ideal material for these applications. Zirconia is used for its transformation toughening properties; yet recent research indicates that the stablization effect, which increases the toughness, degrades after long times at high temperature (50-100 hrs. above 1200°C),[6] and there is a fracture problem with prolonged aging at 200-300°C. Other problems encountered with zirconia liners include a roughening effect in service and difficulties (rupture and cracking) during liner installation. Significant improvements have been made in both the material and engine redesign to better utilize new materials. Chromia and PSZ coatings have had the greatest success to date in engine tests at the current level of development.[7] Materials research continues to provide better properties in existing materials and is developing new materials for specific applications.

The applications which show immediate promise for monolithic ceramics are valve seats, tappets, exhaust ports and turbochargers. These are applications which make use of the good wear resistance of ceramics and their high temperature properties. Valve seats and tappets (wear pads) are both simple and small shapes which can be easily manufactured. Wear pads are currently manufactured from stellite, a high Cr-Co alloy.

Exhaust ports are a more intricately shaped part. A port must be slip cast and green-machined to close tolerances. However, with the higher operating temperatures in the adiabatic diesel, ceramic materials are ideal for both the temperature and erosion wear of the

exhaust gases. The present material being tested for this application is Tialet, an aluminum titanate with insulating ability, reasonable mechanical strength at elevated temperatures, and good corrosion/erosion resistance. The manufacturing technology involved in slip casting, machining, and joining an exhaust port is expensive. However, if the demand for these parts increases from tens and hundreds to tens of thousands, signficant economies of scale could be realized in the production process which should greatly reduce cost. New materials are being examined and incorporated into the present engine design, and modifications are being made to the design to better utilize the material.

Another promising application for ceramics is turbocharger rotors in both reciprocating engines and diesels. In the standard internal combustion engine, a turbocharger increases the power output from the engine and increases fuel economy. Turbochargers function by using exhaust gases to turn a turbine which drives a compressor. The compressor pumps hot pressurized air back into the engine. The turbocharger rotor has been the main target of ceramic materials research because it can withstand the high temperatures of the exhaust gases and has lower rotational inertia, which is due to its lower density (3.2 g/cm^3 for SiC) than that of superalloys (more than 7.5 g/cm^3). The materials being considered are injection molded SiC and Si_3N_4, both of which meet the necessary property requirements and have been selected by different manufacturers for development programs. In reciprocating engines, turbochargers could maximize the power delivered by the engine, minimize the power lag

experienced in automotive diesels, and generate more power at high rpm while improving fuel efficiency. In a diesel engine, turbocharging with turbocompounding (Figure 6.7) provides hot pressurized air for the combustion chamber and additional power to the crankshaft. The turbocharger can help increase the overall performance of the diesel and can reduce the specific fuel consumption by approximately 20%. Turbocharger materials must withstand the stresses generated by transient conditions due to a cold start. Gas temperatures can rise from 20°C to 550°C after a five second idle at 5000 RPM.[8]

The major constraint for ceramic turbocharger use is the current state of ceramic injection molding technology. Injection molded Si_3N_4 turbochargers are currently being manufactured by a company in Japan in lots of 100-500 per month. Within three years, the company plans to increase the number of turbochargers manufactured to 100,000 per month. There are at least another five or six Japanese companies who are planning to manufacture Si_3N_4 or SiC turbochargers. Several U.S. and European companies have also discussed manufacturing plans. Another problem is the non-destructive evaluation of these rotors. Large flaws (larger than 50μm) are the rule rather than the exception with today's technology. Thus, the early entrants into production will use hot isostatic pressing as a final processing step of injection-molded parts. The polymer and resin burnout cycles for these parts are 5-7 days for about ten different companies. Work is underway to reduce the time required (cycle length) for burnout. One company has reduced the cycle to nearly a day for special cases.

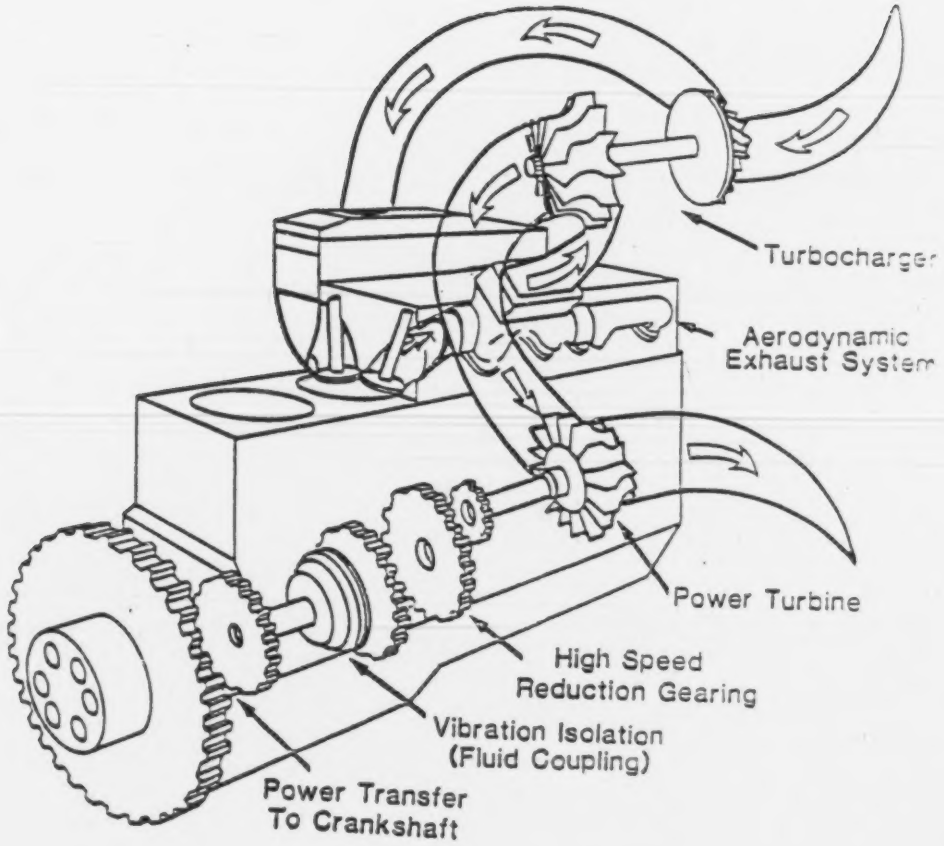


Figure 6.7. Cummins NH turbocompound diesel engine.[9] Hybrid diesel-turbine system in which piston power is supplemented by turbine power recovered from the exhaust gas.

The attachment of the turbocharger rotor to the metallic shaft (Figure 6.8) is also an active area of research. The rotational inertia experienced by the rotor requires epoxy and a pin to cement the ceramic rotor to a metallic shaft outside the hot zone of the engine. Other attachment methods were not as reliable. Although ceramic engine components are not produced domestically on a commercial scale, the Japanese have already begun production of several small ceramic engine components.

Diesel Market Analysis

Overall estimates for the value of ceramics used in heat engines are as high as $750 million by the year 2000, see Table 6.5. This figure includes the value of metallic parts for a number of engine components, many of which are not potentials for ceramic substitution. However, ceramics could replace 5-20% of the metallic components by the year 2000.[10] Currently, no other projections exist that are not based on the direct replacement of metallic parts by ceramics.

Current projections for the market potential of turbochargers are indicated in Table 6.6. The number of ceramic turbochargers will depend upon the fraction of diesels produced. The total dollar value of ceramics for turbochargers will range from 5% to 75% of the automotive market, $15-230 million, by the year 2000.[10] Presently, turbocharger use has been limited to sporty, expensive cars which have a price premium associated with them; therefore, the price of the rotor can easily be incorporated into the price of the car. The

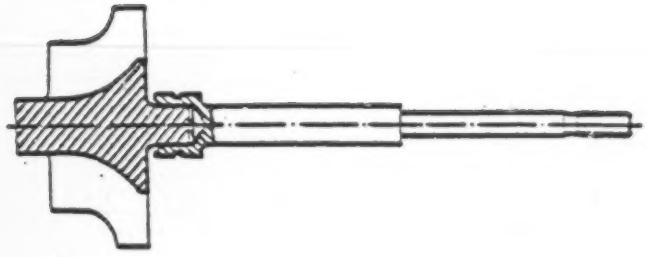


Figure 6.8. Basic design of ceramic rotor and metallic shaft [8]

Table 6.5. Ceramic Market Potential for Heat Engines. (10^6 1981 dollars)*

Year	1977	1981	1990	2000
Diesel, for highway vehicles				
Piston, piston rings, and valves	595	709	1199	1807
Cylinder liners, and head inserts	653	778	1316	1984
5% market penetration				189
20% market penetration				758

* Adapted from Reference 10.

Table 6.6. The Market Potential for Turbochargers. (10^6 1981 dollars)*

Year	1977	1981	1990	2000
Turbochargers	101	120	203	306
in the year 2000		5% market ceramic		15.3
		75% market ceramic		230

* Adapted from Reference 10.

first turbodiesel on the U.S. market was priced $1000 above the conventional model. The cost of the turbocharger and installation ranged from $250 - $400 on this model, showing a high profit margin for the unit.[11] In order for turbochargers to be widely used in the conventional engine, large performance benefits must be demonstrated and the cost must be reduced. Some industry sources indicate that 50% of the market will be turbocharged within the next three years. In order to achieve this degree of market penetration, increased temperature capacity and potentially lower production cost of ceramics are required.

It is possible to say, however, that if 50% of the domestic automotive market is turbocharged (approximately 5 million cars) and if ceramics are used in half those cars, 2.5-3 million pounds of advanced ceramics will be required by 1990. Good quality powders of SiC or Si_3N_4 range in price from $8-$20/lb. Therefore, this application alone has a potential of $100 million for ceramic materials.

The Japanese are currently manufacturing Si_3N_4 turbochargers, glow plugs, and swirl chambers. Trigger prices for these ceramic components are $40-60/lb for the manufactured product. The present cost of producing these parts is over $40/lb, especially for turbochargers and swirl chambers. However, the Japanese hope to reduce the cost of engine components such as piston caps and cylinder liners to $13/lb through better processing. Additional cost reductions would be achieved through cheap, high quality powders. Work is underway to reduce the cost of powder from $20/lb

to $3/lb, the ultimate goal being the production of reliable, reproducible ceramic components for engines at approximately $8/lb. At this price level, as much as 10-12 lbs of ceramics could be incorporated into the engine.[12]

Gas Turbines

There has been a significant amount of publicity recently on the use of ceramics in industrial, automotive, and aircraft gas turbines. As yet, none of these turbines are near commercialized production, but high temperature strength, chemical stability, and light weight do make ceramics potentially viable alternatives to the superalloys and high alloy steels which are presently in use. In fact, the proposed small diameter automobile gas turbine appears to be viable only if ceramic hot section components are used. The major driving forces behind the use of advanced ceramics as substitutes for cobalt and chromium containing alloys in turbine applications are potential price reductions and performance benefits. The availability of strategic and critical materials is also a factor. The use of cobalt and chromium in gas turbines applications is projected to nearly double by 1989 (Table 6.7). The successful development of advanced ceramics for turbine applications would have a significant influence on reducing U.S. demand for these metals, especially cobalt. High tech ceramic components for gas turbines can be made from silicon carbide (SiC), silicon nitride (Si_3N_4), sialons, and alumina silicates, all of which are produced from abundant, non-critical materials available in the U.S.

Table 6.7. Projection of Chromium and Cobalt Use In Gas Turbines (1000 lbs.).*

	Chromium				Cobalt			
	1981	1981** % Total	1985	1989	1981	1981 % Total	1985	1989
Jet Engines								
Shipments+	15800	<1%	14350	15125	4420	38%	4020	4240
Consumption+	3050	"	3425	4450	880	8%	1030	1250
Industrial Gas Turbines:								
Shipments	1750	"	2300	3025	490	4%	640	800
Consumption	875	"	1150	1525	260	2%	320	430
Vehicular Gas Turbines:								
Shipments	525	"	800	925	150	1%	220	260
Consumption	255	"	400	475	80	<1%	110	130

* Adapted from the Bureau of Mines Mineral Profiles for Chromium and Cobalt.

** 1981 % of total is based on the total U.S. domestic consumption in 1981.

+ Shipments of superalloys are often four times higher than actual consumption, especially in the aerospace industry.

The thermal and mechanical requirements for various components of the gas turbine can be satisfied by various ceramic materials (Figures 6.9 and 6.10, Table 6.8). This section describes the state of ceramics research for automotive, stationary, and aircraft gas turbine engines, in terms of material limitations and future development, and provides some preliminary estimates on market size and the cost of producing ceramic gas turbine components.

Automotive Gas Turbines

Current Research

By far the largest research effort concerned with the use of ceramics in gas turbine engines has been funded by DOE/NASA. This program has focused on the development of an automotive gas turbine (AGT) engine. The incorporation of ceramic components into the basic AGT design (Figure 6.11) would allow higher inlet gas temperatures and, therefore, higher fuel efficiencies, theoretically 20% higher than those achievable with a mature, metallic gas turbine (Table 6.9). The AGT engine would not only provide improved fuel efficiencies, but also lower emissions, reduced weight, high durability, and potentially low maintainence.[14] In addition, an advanced metallic engine with a catalytic converter requires at least 2 kg chromium per engine due to both the converter and superalloy content. Researchers believe that a ceramic AGT engine, on the other hand, would require less than 0.5 kg chromium per engine and would not require a catalytic converter, resulting in a lower weight and a reduced need for a strategic metal.[1]

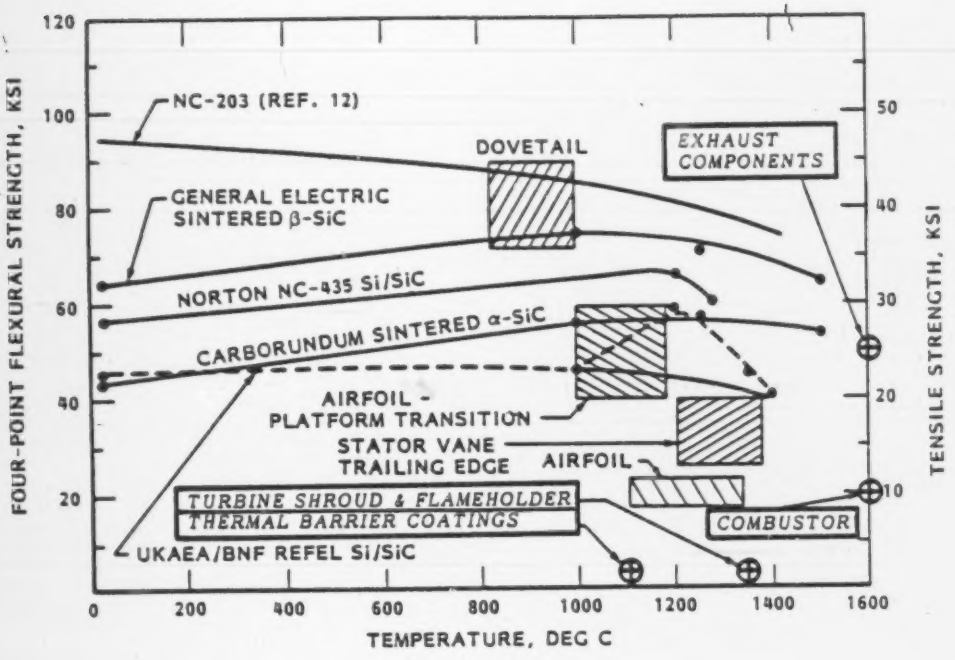


Figure 6.9. Strength of silicon carbide materials vs. required strengths for engine components (with ⊕ requirements for additional components superimposed upon the basic figure).[13]

---

* From Katz, R.N., "Some Aspects of Materials and Structures Engineering with Ceramics for Engine Applications," presented at the Third International Conference on Mechanical Behavior of Materials, University of Cambridge. England, August 20, 1979.

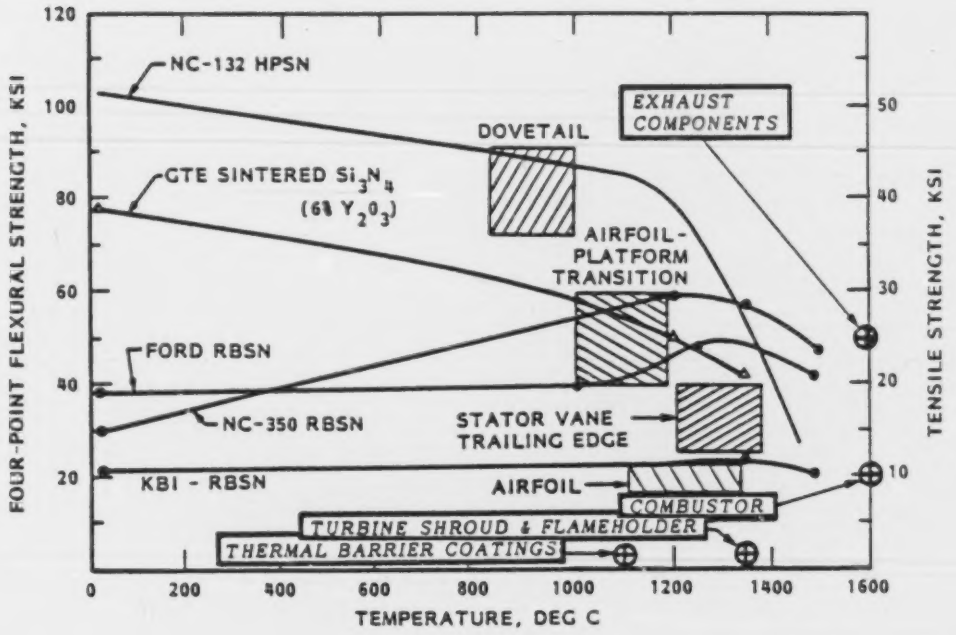
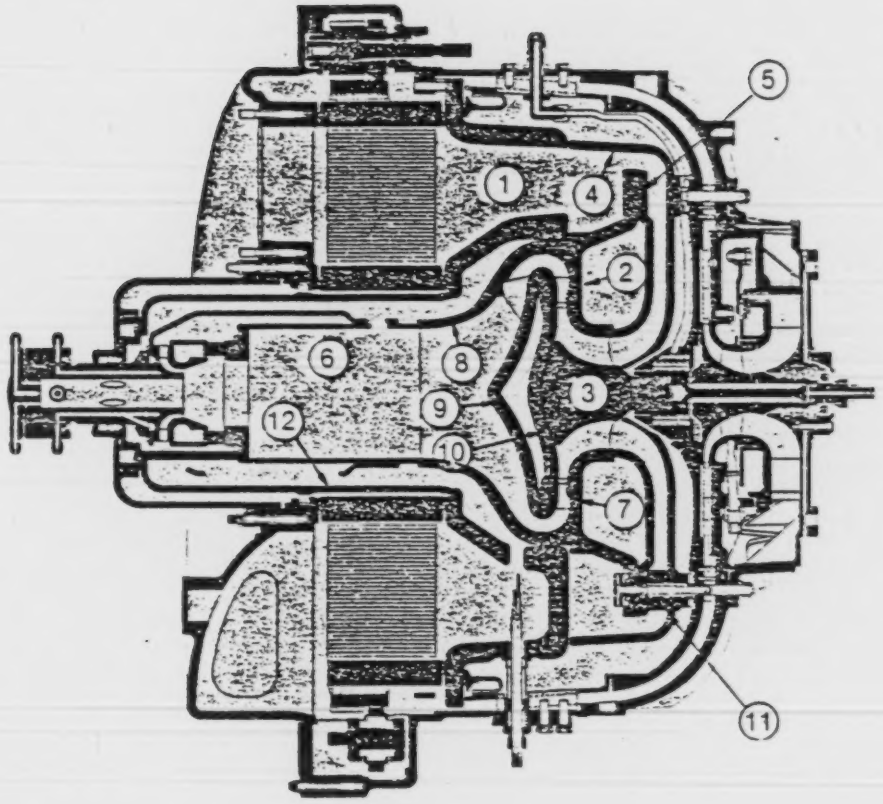


Figure 6.10. Strength of silicon nitride materials vs. required strengths for engine components (with ⊕ requirements for additional components superimposed upon the basic figure).[13]

Table 6.8. Representative Engine Design Requirements For Ceramics Applications [13]

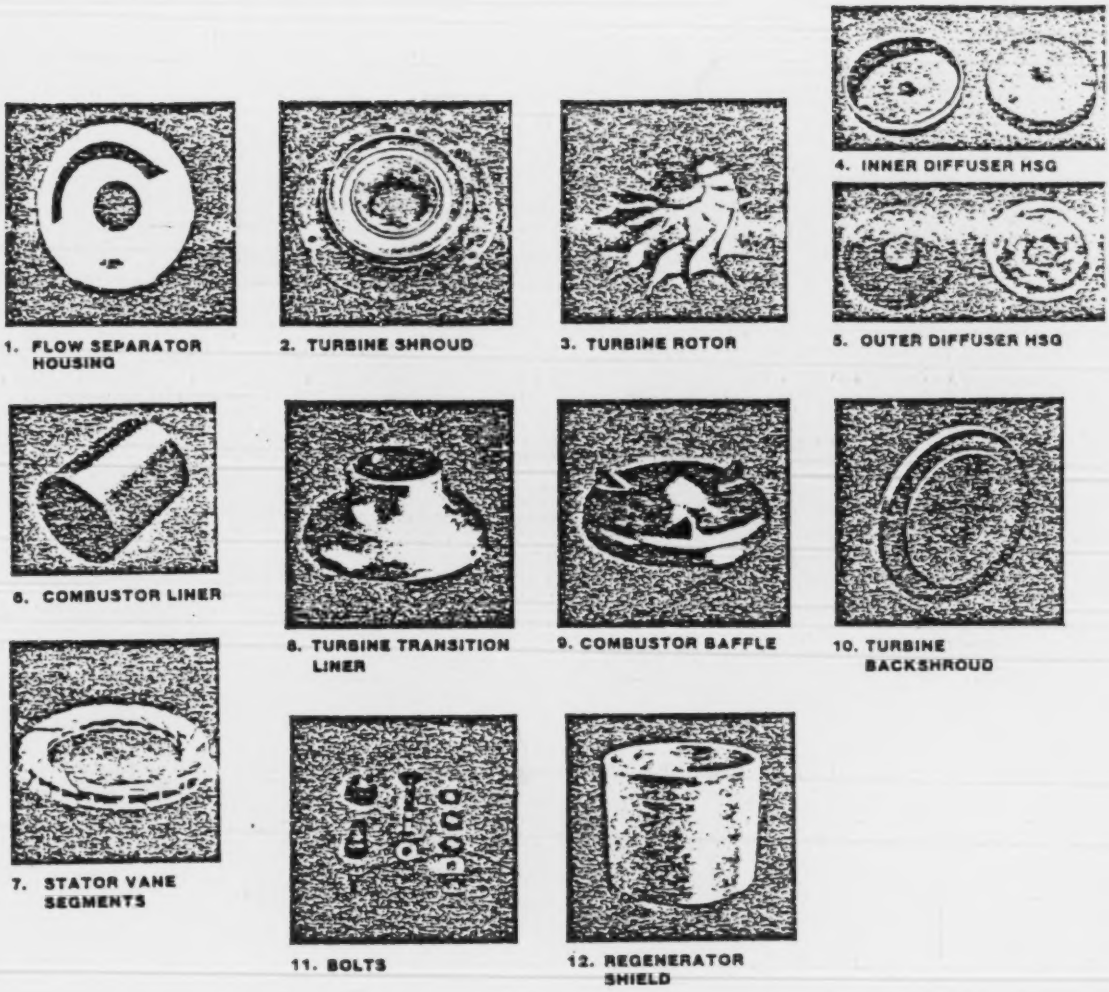
ITEM	TEMP °F	TEMP [°C]	STRESS KPSI	STRESS [MPa]	ADDITIONAL CONSIDERATIONS	HOURS(a)	CYCLES(a)
TURBINE BLADE	1400	[760]	40	[276]	• HIGH CONTACT LOADS BETWEEN BLADE AND DISK • CONTOUR TOLERANCE TO ±.001 IN. FOR SMALL ENGINE AIRFOILS	5000 (35)	15000 (50)
	2000	[1093]	25	[172]			
TURBINE VANE	2000	[1093]	20	[138]	• INTERFACE LOAD CAPABILITY • CONTOUR TOLERANCE SAME AS FOR BLADE		
	2400	[1649]	10	[69]			
TURBINE DISK	1600	[830]	65	[448]	• TEMPERATURE, EXPANSION AND LOAD COMPATIBILITY AT INTERFACE WITH METAL SHAFT		
TURBINE SHROUD	2500	[1371]	(b)		• RESISTANCE TO OXIDATION AND SPALLING UNDER RUB CONDITIONS		
COMBUSTOR	3000	[1649]	10		• HIGH THERMAL TRANSIENT CAPABILITY • COMPATIBILITY WITH FUEL		
AFTERBURNER FLAMEHOLDER	2500	[1371]	(b)		• HIGH THERMAL TRANSIENT CAPABILITY • COMPATIBILITY WITH FUEL	1000	2000
EXHAUST COMPONENTS	3000	[1649]	25	[172]			
THERMAL BARRIER COATINGS	2000	[1093]	(b)		• ADHERENCE INTEGRITY		
BEARINGS	400 lub. 1000 unlub.	[204] [538]	(c)		• DN CAPABILITY 2.5×10^6 mm-RPM	(35)	

(a) Hours and cycles shown in ( ) are for unmanned applications. Other values are for manned applications.
(b) Stress requirements are low for these items.
(c) Stresses are highly localized, Hertzian in character.



1. Flow separator Housing
2. Turbine shroud
3. Turbine rotor
4. Inner diffuser HSG
5. Outer diffuser HSG
6. Combustor liner
7. Stator vane segments
8. Turbine transition liner
9. Combustion baffle
10. Turbine backshroud
11. Bolts
12. Regenerator shield

Figure 6.11. Incorporation of ceramics into the basic design of the gas turbine engine.[4]



	CARBORUNDUM	FORD CORNING	ACC	PURE CARBON	NGK
(1)		LAS			
(2)	α SiC		RBSN		
(3)	α SiC	SRBSN	SSN	RSSC	
(4)			RBSN		
(5)			RBSN		
(6)	α SiC			RSSC	
(7)	α SiC	RBSN	RBSN		
(8)	α SiC		RBSN		SSN
(9)	α SiC		RBSN		
(10)	α SiC				SSN
(11)	α SiC		RBSN		
(12)	α SiC		RBSN		

CERAMIC MATERIALS

SiC = Sintered alpha silicon carbide
LAS = Lithium Aluminum Silicate
SRBSN = Sintered Reaction Bonded Silicon Nitride
RBSN = Reaction Bonded Silicon Nitride
SSN = Sintered Silicon Nitride
RSSC = Reaction Sintered Silicon Carbide

Figure 6.11. Incorporation of ceramics into the basic design of the gas turbine engine.[4] (Cont'd)

Table 6.9. Comparison of Automotive Gas Turbine Engines.[1]

	Current	Mature Metallic	Advanced Ceramic
Maximum turbine inlet temperature (°C)	1,135	1,160	1,525
Maximum regenerator* inlet temperature (°C)	795	1,100	1,220
Efficiency (%)	26	33	46
Engine weight (kgs)	272	166	132
Fuel consumption (mpg)			
Compact car			
City driving	...	23	32
Highway driving	...	33	46
Full-size car			
City driving	9	19	...
Highway driving	...	28	...

* Heat exchanger between exhaust gas and incoming air.

The AGT components for which ceramic materials may be substituted are indicated in Figure 6.11. The ceramic materials used have included two forms of SiC, three forms of Si_3N_4, and lithium aluminum silicates (LAS). These materials have survived various initial non-destructive evaluation (NDE) testing procedures and simulated engine conditions, thus demonstrating the engineering feasibility of advanced ceramics for these applications. Ceramic parts have been tested unassembled to 1150°C and assembled to 870°C. Bladed rotors were spin-tested at 115,000 rpm. Future work will involve testing these materials in actual engine test rigs.[14]

In order to progress from a prototype to a commercial manufacturing process, more efficient, reliable, and reproducible methods of manufacturing ceramic parts are needed. Three methods being researched are injection molding, dry pressing, and slip-casting of AGT components. Both injection molding and slip casting provide a means of forming intricately shaped ceramic parts with a minimum of machining. Machining and inspection are by far the biggest portions (38% and 51%, respectively) of the total cost of a ceramic part manufactured by injection molding (Figure 6.12). This high cost of machining provides an incentive for the further development of near-net shape component fabrication processes. The fact that inspection costs are so high for the fabrication of a ceramic part as opposed to those for a metal blade indicates the need for improvements in the reliability and reproducibility of ceramic components, as well as a need for better non-destructive evaluation techniques.

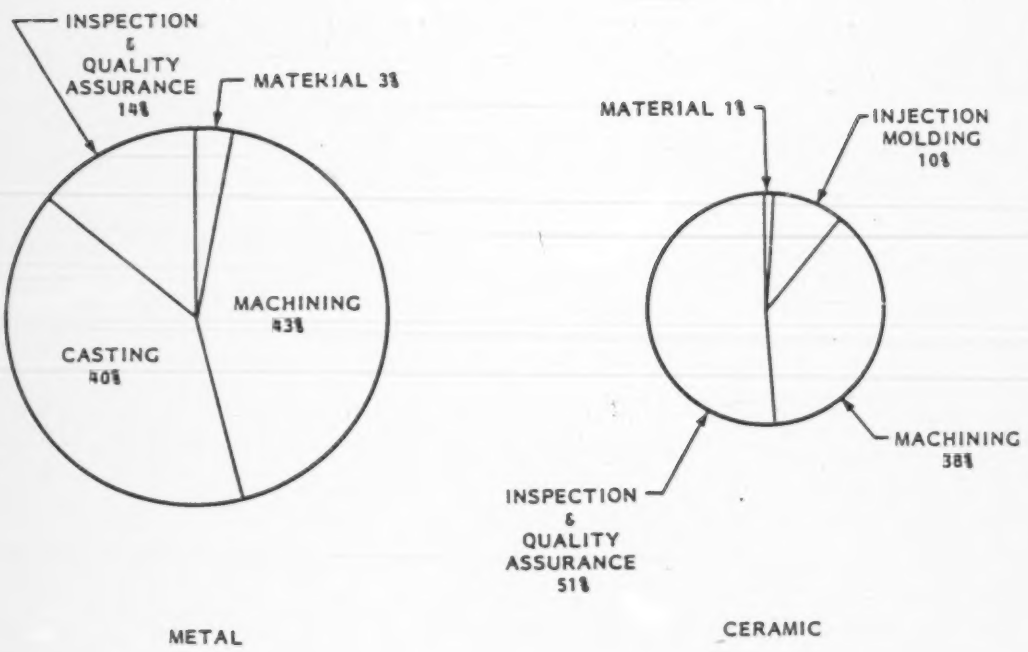


Figure 6.12. Turbine blade cost comparisons: aircooled metal vs. uncooled ceramic.[13]

Experimental Materials and Parts

Two potential ceramic materials substitutes for metallic components in automotive gas turbines, SiC and Si_3N_4, and their properties are listed in Table 6.10. Both of these materials have good high temperature strength, thermal shock resistance, and oxidation resistance. However, there are significant differences between these two materials.[15] Silicon carbide has less low temperature strength and lower thermal shock resistance than Si_3N_4. However, it has a greater high temperature strength and is more creep resistant than is Si_3N_4. Silicon carbide also has a higher thermal conductivity and thermal diffusivity than Si_3N_4. Therefore, at temperatures greater than 1400°C, SiC is superior to Si_3N_4 and might be the better candidate as a combustor material in a gas turbine engine. A more general comparison of the properties of SiC with those of Si_3N_4 is presented in Table 6.11.

These two materials have been used to fabricate various turbine hot section, stationary, and rotating parts including scrolls, vanes, ducts, rotors, combustors, and regenerators. Many of these parts have been made from both SiC and Si_3N_4 in an effort to determine at the experimental stage which material and processing technique performs best.

There is a significant difference between materials properties measured in the laboratory and those exhibited in a final prototype or component. Much of the data collected on ceramic material properties result from laboratory tests in which the properties being evaluated do not always represent those attainable in a final

Table 6.10. Typical Properties of Silicon Carbide and Silicon Nitride Ceramics [16]

Type	Bend strength (four-point) (MPa)			Young's modulus (GPa)	Coefficient of thermal expansion, α (10^{-6} °C^{-1})	Thermal conductivity, K (W m^{-1} °C^{-1})
	RT*	1000°C	1375°C			
Silicon carbides						
Hot-pressed (Al_2O_3 additive)	655	585	520	449	4.5	85–35
Sintered (α phase)	310	310	310	407	4.8	100–50
Reaction-sintered (20 percent free Si by volume)	380	415	275	345	4.4	100–50
SiC fiber–Si composite	275	275	275	340		70
CVD†	415	550	550	414		
Silicon nitrides						
Hot-pressed (MgO additive)	690	620	330	317	3.0	30–15
Sintered (Y_2O_3 additive)	655	585	275	276	3.2	28–12
Reaction-bonded (2.45 g/cm^3)	210	345	380	165	2.8	6–3
β'-SiAlON (sintered)	485	485	275	297	3.2	22

*Room temperature. †Chemically vapor-deposited.

Table 6.11. A Comparison of Major Characteristics of Dense Forms of Silicon Carbide and Silicon Nitride.[15]

Silicon Carbide	Silicon Nitride
• Intermediate Strength	• High Strength
• High Thermal Expansion	• Low Thermal Expansion
• Poor Thermal Shock Resistance	• Good Thermal Shock Resistance
• Low Fracture Toughness	• Higher Fracture Toughness
• High Temperature Stability	• Strength Degradation by Slow-Crack Growth
• High Thermal Conductivity	• Low Thermal Conductivity
• Good Oxidation Resistance	• Oxidation Strong Function of Impurities
• High Creep Strength	• Low Creep Strength
• Low Influence of Impurities	• Second Phases Influence Behavior
• High Elastic Modulus	• Lower Elastic Modulus
• Transgranular Fracture	• Intergranular Fracture
• Little Subcritical Crack Growth	• Nonlinear Stress-Strain

part. Material properties also vary between manufacturers and depend strongly on the dopants added, powder processing technique, and part fabrication method. High density fabrication techniques (dry pressing, injection molding, and hot pressing) often yield components with superior properties compared with those produced from lower final density fabrication processes (slip casting, Table 6.12). Slip casting processes have a lower, overall cost and may be used to manufacture small volumes of parts or specialty shapes.

In addition, there is a substantial variation in the properties of advanced ceramics due to non-uniform and as yet uncontrolled microstructural flaws and imperfections. This situation is further amplified by the inherent brittle failure mode of structural ceramics. Ceramics fail in a brittle manner, a process with little or no plastic deformation. In crystalline materials, fracture occurs along certain crystallographic axes or along grain boundaries. At high temperatures, fracture may occur intergranularly. The theoretical strength of a body is calculated from the energy required to separate two adjacent planes of atoms. Theoretical strength predictions for most ceramics yield values in the order of 10^6 psi. However, actual strengths are much lower. Actual strength can be calculated from Griffith crack theory, which suggests that flaws within the material can act as stress concentrators. From this theory, it follows that the fracture strength of a brittle solid is statistical in nature. The actual strength of the material depends on the probability that a flaw of the size required to initiate fracture at an applied stress level is

Table 6.12. Differences in the Properties of High Performance Ceramics Produced by Slip Casting, Hot Pressing, and Reaction-Bonding.[17]

	Slip Casting	Hot Pressing			Reaction-Bonding
Composition	85v/o SiC 15v/o Si	SiC (Al)	Si_3N_4 (MgO)	Si_3N_4 (Y_2O_3)	Si_3N_4
Grain Size (μm)	<150	<10	<3	<3	<3
Bulk Density (g/cc)	3.10	3.30	3.21	3.30	2.50
Total Porosity (%)	<1	<1	<2	<2	<23
Thermal Conductivity (W/m•k at RT)	135	94	32		~8
Thermal Expansion Coefficient ($x10^{-6}$ °C^{-1})	4.9	4.2	3.5		~3.5
ΔTc (Hasselman) (°C)	275	560	770	950	420
Young's Modulus (GN/m^2)	385	437	320	310	172
Fracture Toughness ($MN/m^{3/2}$)	3.5	4.0	5.5		1.4
Transverse Rupture Strength - 3 pt. (MN/m^2)					
RT	305	725	800	1020	360
500°C	300	655	800	1000	
1000°C	280	600	715	950	350

present. Therefore, the theory predicts a wide range of strengths depending upon the overall homogeneity of the body. Experimental results have illustrated that the strength of most ceramics is also dependent upon the failure mode which is related to the surface area and volume placed under maximum stress. The broad statistical nature of ceramics failure behavior can be somewhat mitigated with the selection of component designs aimed at reducing stress concentration. Several important ceramic design considerations are illustrated in Figure 6.13.

Ideally, advanced ceramic components could be used as direct substitutes for metal parts. However, such direct substitution is constrained by the current limited capacity to join ceramic-to-ceramic and ceramic-to-metal parts. This is due primarily to the thermal expansion coefficient mismatch between many metals and ceramics and the lack of ductility on the part of ceramics which restricts the ability of ceramics to accommodate the thermal expansion mismatch. Consequently, care must be taken to select materials and a component design which accommodates the thermal expansion and ductility of the materials involved. Ceramics can be brazed, welded, or epoxied to various metals and other ceramic materials. However, the practical operating temperature range of such joined components are limited somewhat by the joining technology.

Ceramics will probably first be used in gas turbines as thermal barrier layers or coatings over refractory metals. This use provides both temperature and oxidation/corrosion resistance for the

Reasons

Edge chamfering is the most important design consideration when using non-ductile materials. Chipping resistance increases dramatically when the edge is radiused or changed from 90° to 135° (i.e., 45° chamfer).

Avoid thin flanges and sharp contact areas. Use generous radii for fillets at all intersecting surfaces to minimize point loading.

When bonding or pressing into a metal housing, avoid Hexoloy SiC protrusions, especially when a heat-shrink assembly is employed.

Avoid inside diameter grooves or notches. It is much more economical to grind grooves or notches on the outside.

Avoid expensive external projections due to high cost in fabrication. Use notches, slots or grooves.

Avoid notches or grooves which can interfere with bearing loads. Notches should be placed in the unloaded position. This procedure also assists in keeping wear debris away from the bearing surface.

Avoid bearing lengths exceeding two times the inside diameter. Instead, use two or more bearing components.

For anti-rotation or drive pins, through slots are preferred over blind holes or slots for economical reasons.

Avoid undercut geometries.

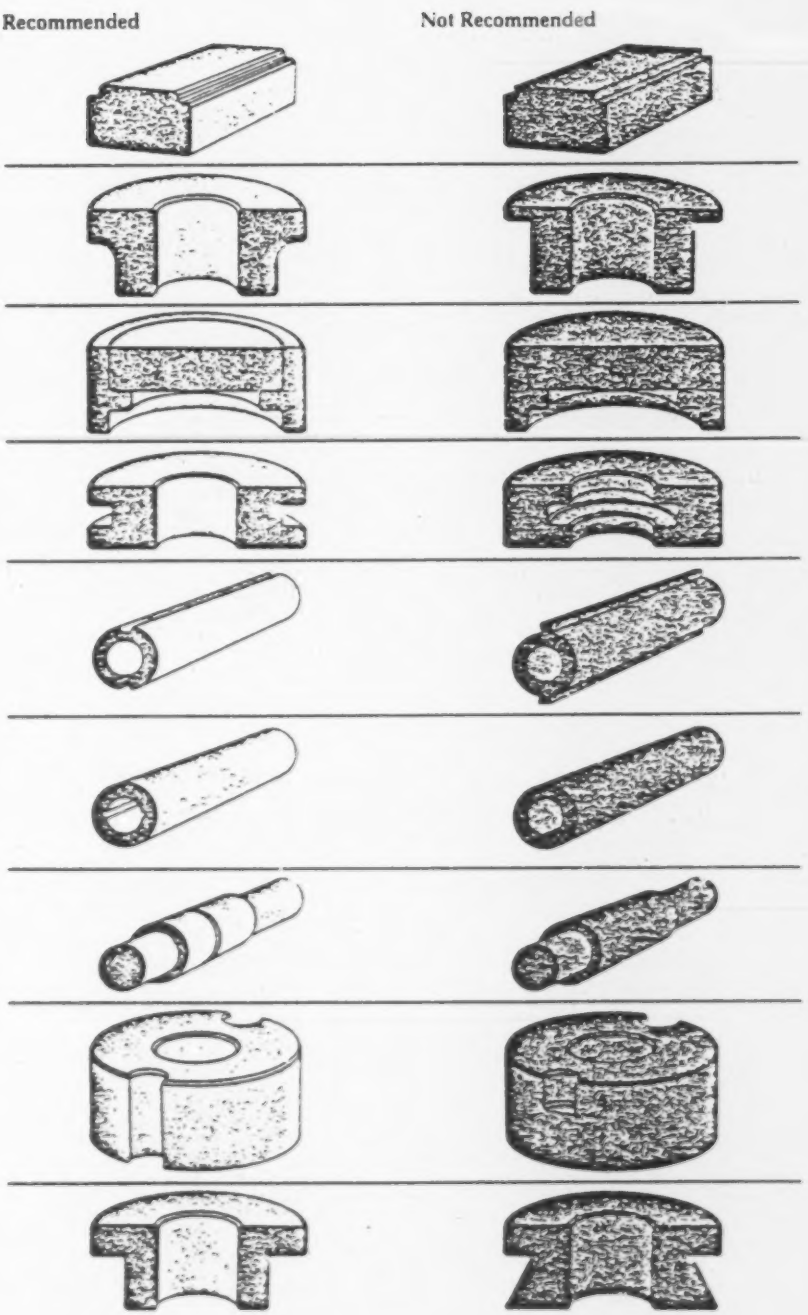


Figure 6.13. Redesign of ceramic parts to reduce stress concentrations.[18]

metallic component. Coatings can reduce the quantity of metal required and increase the lifetime of the component. Ceramic usage in turbines may then progress to monolithic stationary parts, such as nozzle vanes, and can be expected to eventually replace hot moving parts such as the turbine blades. The most probable configuration for a ceramic turbine blade is a small, short blade designed to reduce stress concentrations at the joint.

Aircraft and Stationary Gas Turbines

The feasibility of ceramics use in automotive gas turbines has been demonstrated and publicized.[4] Research into other gas turbines is also underway. Figures 6.9 and 6.10 illustrate the material requirements for aircraft turbines. In many cases, ceramic materials are well suited to the application which include airfoils, stator vanes, shrouds, and thermal barrier coatings. However, technical barriers in the powder processing and component fabrications technology, economic barriers due to the high cost of prototype parts, and institutional barriers have slowed the progress of ceramic parts development for these applications. Approval for materials for manned aircraft parts takes time, and, with the current technology, it is not entirely clear that ceramics are technically or economically viable material alternatives to superalloys.

Reliability and reproducibility are strict requirements of aircraft engine materials, with lifetime requirements per part ranging up to 10,000 hours. Turbines with superalloy components,

requiring air and water cooling of parts, theoretically have a maximum operating inlet temperature of 1600°C. This maximum inlet temperature has not yet been achieved in commercial turbines. At the present time, gas turbine inlet temperatures range as high as 950°C-1050°C. Ceramics technology could increase the maximum inlet temperature to at least 1800°C. This would provide significant increases in energy efficiency with attendant cost savings. However, as with the automotive turbine engine, the aircraft turbine engine must be redesigned in order to accommodate ceramics and take full advantage of their high temperature performance.

Ceramics may also be used in stationary turbines for power generation. Stationary turbines require even longer component lifetimes, as high as 30,000 hours. The most probable use for ceramics in this capacity would be accessory power units (APU), which are used only during peak periods or emergencies. However, aircraft and stationary turbines are large; thus, the statistical problem of flaws make large components more difficult to fabricate.

Ceramic components have been fabricated for all three types of gas turbine engines, demonstrating that it is feasible to use ceramics for many of the hot section parts. Ceramics in APU's would not be as susceptible to the fatigue and erosion which are major problems with metallic alloys. However, the current state-of-the-art technology requires significant research and development efforts to provide inexpensive, reliable, and reproducible ceramic components. Table 6.13 indicates that these development efforts, although risky, have a significant potential financial benefit.[1]

Table 6.13. Aircraft Gas Turbine Engines: Estimated Worth and Development Costs in 1977 Dollars.[1]

Component	Estimated Worth* (US$ million)	Estimated Development Cost (US$ million)
Vanes	66.6	6.0
Shrouds	34.2	3.3
Combustor Liner	5.7	3.0

* Calculated as the value of ceramic components when applied to a total 100 aircraft fleet over a 15-year aircraft service period. Other estimates indicate a material with 1800°C temperature capability costing 50% more than the current metal alloy would yield an engine 3% higher in cost, 1.2% more fuel efficient, and would reduce overall operating cost by 0.18%.

Economics and Market Size of Gas Turbines

The gas turbine market available for possible penetration by ceramic components penetration is divided into three main sectors: automotive, civil aircraft, and electric power generation. The primary focus of ceramic gas turbine research has concentrated on the automotive sector due to the potential large volume of AGT sales (Table 6.14). Stationary gas turbines also present an opportunity for the use of ceramic parts; however, this application requires parts with a longer life and extremely high reliability. An even longer-term potential is the use of ceramics in aircraft gas turbine engines. This is, once again, a high priced, potential market, but many technological advances are necessary to insure the operational reliability of advanced ceramics in this application.

Automotive Gas Turbines

A range of market predictions have been made for ceramic parts in vehicular engines. These estimates are based on the value of the replacement of metallic parts with ceramics in all vehicular heat engines (Table 6.15). Department of Commerce statistics from 1983 indicate that for bearings, roller bearings, cylinder heads, cylinder liners, wear parts, pistons, piston rings, engine intake and exhaust valves, and turbochargers, the value of all metal parts was over $3 billion.[10] Reciprocating engines make up the major portion of automotive sales. Thus far, diesels have penetrated the market at less than 6.5% while gas turbines have had an almost negligible market share.[19] In Europe, the diesel market share is

Table 6.14. Features of Gas Turbine Engines by Application (Domestic Market).[1]

Application	Size (Rotor diameter)	Power level	Life (hours)	Market Volume Potential (number pa)
Electric Power Generation	<80 inches	20 - 100 MW	30,000	200
Civil Aircraft	<30 inches	15,000 - 50,000 lbs. thrust	<10,000	3,500
Automotive	<5 inches	100 - 200 hp	3,500	10 million

Table 6.15. Summary of Market Potential for Selected Ceramic Parts (1981$ x 10^6).[10]

Applications	1977	1981	1990	2000
Diesel/Gas Turbine components for highway vehicles				
Piston, piston rings, and valves	$ 595	$ 709	$ 1199	$ 1807
Cylinder liners and cylinder head inserts	653	778	1316	1984
Bearings				
Taper roller, nontaper roller, mounted bearings, rollers, and spare parts	2099	2502	4232	6379
Turbochargers	101	120	203	306
Gas turbines, except aircraft	148	176	298	449
Total	$ 3596	$ 4285	$ 7248	$10,925

closer to 10% of the automotive market. Ceramic components can be used in all three engine types: AGTs, diesels, and internal combustion engines.

The benefits of the automotive gas turbine engines include the ability to use a range of fuel types, lower emissions, and higher fuel efficiencies. The automotive gas turbine engine could potentially require 27% less fuel than a comparable horsepower reciprocating engine. This higher fuel efficiency is directly attributable to the use of uncooled ceramic components which allow the engine to operate at a higher inlet gas temperature and burn cleaner. If automotive gas turbines prove to be significantly more efficient than the standard reciprocating engine, fuel prices increase considerably, and/or standard gasoline becomes unavailable, it is possible that automotive gas turbines will gain a substantial market share. A plausible scenario based on a number of estimates, assuming that the technical problems currently encountered in ceramics usage can be overcome, would result in a 12% penetration of ceramic parts into gas turbine/diesel engine parts market by 2005.[20]

Even with the current amount of funding and research in the area of automotive gas turbines, it is unlikely that any turbines containing ceramic components would be commercially available before 1995. Research into materials processing techniques, manufacturing processes, joining technology, non-destructive evaluation, and reliability/quality assurance techniques is required before the automotive gas turbine can become a commercial reality.

Stationary Gas Turbines

Two primary and technical requirements for an economical stationary gas turbine are a minimum turbine inlet temperature of 1350°K with a heat exchanger efficiency of 0.85%. Specific fuel consumption must be below 0.20 Kg/Kwh and the specific power at least 250 Kw/Kg.[13] Here again, ceramics in the hot section and recuperator allow higher inlet temperatures which result in higher fuel efficiencies. The high temperatures possible with ceramics are as good or better than those attained by high temperature, cooled superalloys. The market for industrial gas turbines for power generation is extremely dependent on the total electrical energy required in the United States. Accessory power units (APU) are also a potential area for ceramic use in gas turbines.

Based on estimates for the total amount of energy demanded, ceramic parts sales for use in electricity generating turbines could be as high as $2 billion by the year 2010.[20] A summary of some projections of energy consumption in this country and the estimated substitution of ceramic parts into these gas turbines is included in Table 6.16. Again, these estimates are based on ceramics replacing metal parts in a number of applications, not all of which are realistic at the present level of ceramic technology.

Recent research examined the cost of replacing a specific turbine component, a metal vane nozzle with a ceramic vane nozzle, see Table 6.17. This is an application in which ceramic materials have been tested and proved to be feasible, with work now underway to reduce the cost of fabricating the ceramic part.[21] The metal

Table 6.16. The Market for Ceramic Parts in Stationary Gas Turbine Electric Generators -- Forecast C Highly Probable Scenario.[20]

	1983	1985	1995	2005	2010
Gross national product ($ trillion)	$ 3.5	$ 4.3	$ 11.1	$ 25.3	$ 29.2
Total demand for all energy (quads)	81.0	84.0	90.0	110.0	130.0
Net amount of imported energy (quads)	11.0	10.0	5.0	2.0	Nil
Capital expenditures by public utilities for new plant and equipment ($ billion)	$43.3	$54.0	$139.0	$328.0	$437.0
Penetration of ceramic parts for stationary turbines					
Small power generation	--	--	15.0%	25.0%	30.0%
Large power generation	--	--	5.0%	8.0%	12.0%
Estimate of sales for ceramic parts ($ billion)	--	--	$0.6	$ 1.7	$ 2.1

Source: Based on U.S. Department of Commerce data.

Table 6.17. Ceramic Vane Estimated Production Costs (1981 Dollars --100 Percent Yield Assumed and Inspection Cost Not Included) [21]

Vendor	Material	Process	Cost Estimate 1000 Vanes	Cost Estimate 10,000 Vanes	Nonamortized Costs
A	$HPSi_3N_4$	Press to near net shape, slice & grind	13.36	13.36	Tooling costs amortized in quote
B	Sintered Si_3N_4	Injection mold then fire	28.80	23.00	$13,355 tooling cost
C	Sintered SiC	Slip cast, then fire	9.76/ 12.78*	8.36/ 10.86*	Tooling costs amortized in quote
D	Siliconized SiC	Slip cast bar, fire and slice	5.50– 6.50	2.00– 2.40	$750-1000 non-recurring engineering charge for 1000 vane order. $2000-3000 for 10,000 vane order.

*Difference is for different vane designs. Lower cost is for vanes with larger trailing edge radius: higher is quote for vanes with the smaller trailing edge radius.

casting that the ceramic replaced was MAR-M421, an alloy consisting largely of chromium and cobalt. Because of the benefits possible through the use of ceramics, the ceramic cost was aimed at 150% of the cost of the metallic component (Table 6.18). Four different materials and manufacturing techniques were used to produce the ceramic nozzle. All estimates, except for the hot pressed Si_3N_4 which required expensive tooling and machining, appeared cost effective. The estimates were based on 100% yield and inspection costs were not included. Inspection is an added cost and requires additional time, equipment, and labor in the manufacturing process. Although most high technology ceramic processes do not achieve high yields, future development should increase process efficiency and the final product should prove cost competitive. Many techniques for materials inspection and quality control have been developed. However, more work is required to provide adequate non-destructive evaluation techniques which can be implemented cost effectively on a production line.

Aircraft Turbines

The potential market for ceramic components in aircraft jet engines has been estimated at over $110 million, based on the number of vanes, shrouds, and combustors required for an entire fleet over a 15-year aircraft service period.[1] Other estimates show a similar value or cost savings. Higher fuel efficiencies and an estimated total investment on the order of $12 million yield a cost/benefit ratio of approximately 10 to 1.[16] Although the use of

Table 6.18. Cost Summary for Fabricating Ceramic Vane Nozzle.[21]

Current (1980) invoice cost of MAR-M421 castings	$293				
Current estimated dollar cost of machining, plating, assembly, brazing, and final machining standard nozzle (quantities >50 nozzles)	$350				
Subtotal	$643				
Additional manhour cost added to assembly process ($25/Hour)	$ 25				
	1	2	3	4	5
Manufacturing method for ceramic vane recesses	Original limited quantity	Multiple copper tungsten EDM bars no rear shroud change	Same as 2 but modified bear shroud	Multiple punch throw away copper electrodes no rear shroud casting changes	Same as 4 but modify rear shroud
Manhour cost for manufacturing recesses ($25/Hour)	$ 408	$113	$108	$ 91.5	$ 85.5
Cost of ceramic vanes	$HPSi_3N_4$ $120 × 15	$HPSi_3N_4$ (Vendor A) $13.40 × 15 = $201			
Total estimated cost of ceramic vane nozzle	$2,876	$982	$977	$961	$965
	Project Goal 150% × 643 = $964				

ceramics in aircraft turbines may lead to a potentially large savings, an immense increase in the reliability of ceramics parts is necessary to first overcome the technical and institutional barriers to the use of ceramics in manned aircraft engines.

Due to the statistical nature of ceramics strength, the current technology is too risky for manned-aircraft. Manned-aircraft would require a material with a high impact strength. Catastrophic failure due to impact make ceramics untenable as jet engine materials at the present level of technology. However, the development of ceramic materials for AGT's and APU's should provide powder processing and manufacturing techniques, as well as a property/performance data base, which would carry over into the aircraft materials market.

Summary

A large potential exists for ceramics in diesel engine applications. To date, research has focused on the use of zirconia monolithic forms or coatings for insulation. Prototype diesel engines have demonstrated the feasibility of ceramics and their performance advantages. Valve seats and wear pads are applications that are well suited to currently available ceramic materials. However, no commercial uses of ceramics in diesels are being marketed by domestic manufacturers.

Estimates of the potential market indicate that almost three quarters of a billion dollars would be spent on ceramic parts in diesels by the year 2000. A $100 million market potential exists

for SiC or Si_3N_4 turbochargers in the next five years. As the technology develops (for example, the development of specialized slip cast parts for exhaust ports and injection molded turbocharger rotors) economies of scope should expand the use of ceramics within the engine and to other markets. The realization of ceramic potentials will be highly dependent upon the materials themselves, fabrication techniques, and finally cost. The performance advantages attainable with ceramic parts may allow their initial introduction at slightly higher cost; however, economies of scale through greater numbers of parts fabricated will be required to reduce the cost to competitive levels.

The driving force for the use of ceramics in diesel and internal combustion engines will not be the replacement of critical materials. While ceramics do have the potential to replace strategic metals by indirect methods; this will not be the primary driving force for their use in engines. In the automotive market, materials are introduced because of performance and cost benefits. Ceramics in diesels would replace insignificant amounts of chromium, cobalt, and manganese. However, an increase in the diesel market through better performance could indirectly reduce the amount of platinum. Adiabatic diesels may not require a catalytic converter, eliminating a primary use of platinum. Turbochargers, if they are not made from ceramics, would require high temperature alloys, increasing the demand for cobalt and chromium.

The potential technical and/or economic viability for ceramic use in the gas turbine engine has been demonstrated. Ceramic

properties such as high temperature strength, corrosion/erosion resistance, and thermal conductivity make them attractive materials for this use. Further research and development are required in both powder processing and component manufacturing techniques before the commercial incorporation of ceramics into these markets is possible.

Current projections indicate that ceramic use will begin to penetrate the small, non-aircraft market in the next 10-15 years, with the large stationary and aircraft turbine markets available for penetration later. As several manufacturers work to reduce the current cost of ceramics for these applications, economies of scale and scope can be expected. Attempts are also being made to familiarize consumers with ceramic capabilities and design in order to lower some of the institutional barriers to market entry. Although research into new materials in gas turbine applications is a continuous process, the industry is conservative in materials selection due to the high development cost associated with a new engine (approximately $1 billion). Ceramics have yet to be accepted as a general substitute by engineers and designers for many metallic applications.

REFERENCES

1. "The Economics of Silicon Ceramics (Silicon Carbide, Silicon Nitride, and the SiAlONs)," 1st ed. (London, England:Roskill Information Services Ltd., November, 1981).

2. Riddell, F.R., Werdhimer, D.D., and Jorden, D.J., "The Development of High-Temperature Materials for Military Engines," DARPA Report, IOA Paper P-1662, Institute of Defense Analysis, Science and Technology Division, Feb. 1983.

3. Larsen, D.C., and Adams, J.W., "Property Screening and Evaluation of Ceramic Turbine Materials," Report, ITT Research Institute, Materials and Manufacturing Technology Division, Chicago, IL, Contract F33615-79-C-5100, 1981.

4. Bryzik, W., and Kamo, R., "TACOM/Cummins Adiabatic Engine Program," SAE-830314, Warrendale, PA, 1983.

5. Kamo, R., "High Technology Ceramics for Japanese Heat Engines," Draft, National Science Foundation, Division of Policy Research Analysis, Advanced Technologies and Resources Policy Group, April 1983.

6. Schioler, L., and Katz, R.N., Army Materials and Mechanics Research Center, Watertown, MA, Personal Communication, June 1983.

7. Kamo, R., Cummins Engine Co., Personal Communication, July, 1983.

8. RottenKolber, P., Langer, M., Storm, R.S., and Frechette, F., "Design, Fabrication, and Testing of an Experimental Alpha Silicon Carbide Turbocharger Rotor," SAE-810523, Warrendale, PA, 1981.

9. Wong, V.W., and Chu, A.C., "New and Advanced Diesel Engines from Cummins Engine Company," Paper submitted to Automotive Engineering Seminar, Tenth Year Anniversary of ITRI, Columbus, IN, June 27 - July 1, 1983.

10. Johnson, L.R., Teotia, A.P.S., and Hill, L.G., "A Structural Ceramics Research Program: A Preliminary Economics Analysis," Report, Center for Transportation Research, Energy and Environmental Systems Divisions, ANL/CNSV-38, 1983.

11. Rubinger, B., "The Bennett File (B): The Strategic Management of New Engine Technology," Harvard Business School, Presidents and Fellows of Harvard College, 1982.

12. Bowen, H.K., "Technology Base for Japan's Ceramic Thrust," Unpublished report draft, MIT, August 1983.

13. Brooks, A., and Bellin, A.I., "Benefits of Ceramics to Gas Turbines," presented at Conference on Ceramics for Turbine Engine Applications, AGARD, Cologne, Germany, October 8-10, 1979.

14. "AGT 101 - Advanced Gas Turbine Program Summary," Report, Garrett/Ford Company, NASA Contract DEN3-167, 1982.

15. Bortz, S.A., and Larsen, D.C., "Properties of Structural Ceramics," presented at 4th Annual Conference on Materials for Coal Conversion and Utilization, National Bureau of Standards, Gaithersberg, MD, October, 1979.

16. Katz, R.N., "High-Temperature Structural Ceramics," Science, Vol. 208, May(1980): 841.

17. Norton Company, High Performance Ceramics Division, Information brochure, 1983.

18. "Hexoloy" High Performance Engineered Silicon Carbide," Design Brochure, Carborundum, 1982.

19. "Percent of Factory-Installed Equipment on U.S. Cars," Wards Automotive Reports, Detroit, MI, July, 19, 1982.

20. "High Technology Industrial Ceramics - A Business Information Report," Report, FIND/SVP, The Information Clearinghouse, New York, June, 1983.

21. Arnold, J.P., McGovern, W., Russell, A.D., and Napier, J.C., "Manufacturing Methods for Erosion Resistant Ceramic Nozzles for Small Gas Turbines," Journal of Engineering for Power, ASME, 82--GT-160, New York, 1982.

22. Katz, R.N., and Lenoe, E.N., "Ceramics for Small Airborne Engine Applications," presented at Ceramics for Turbine Engine Applications Conference, AGARD, Cologne, Germany, October 8-10, 1979.

23. Katz, R.N., "Structural Ceramics for Heat Engines, Future Prospects," Preliminary Draft, Army Materials and Mechanics Research Center, Watertown, MA, 1983.

7. CUTTING TOOLS

Introduction

Carbide cutting tools account for 45% of the $2.25 billion U.S. cutting tool market. The production of cobalt cemented tungston carbide (Co-WC) cutting tools accounts for 9% of total U.S. cobalt consumption. The strategic availability and price instability of cobalt is at present a minor driving force for alternative cutting tool materials. The need for productivity improvements in metal finishing operations stimulates the ongoing development and application of substitute materials. Ceramic cutting tools are emerging as a potential large scale substitution candidate. However, no one material meets all cutting requirements in all applications.

Cutting Tool Development

The primary driving force behind the ongoing research and development of cutting tools is the pressing need to improve productivity. Automotive and aircraft industry engineers gauge productivity in terms of cutting speeds. As a result, the trend towards higher cutting speeds has become the target of tool makers, machine tool builders, and users.

Metal finishing productivity, measured by available cutting speeds, has increased exponentially since the turn of the century (Figure 7.1). Ceramic coated and monolithic ceramic cutting tools have contributed significantly to these increases in cutting speed. However, the tendency has been to develop these new cutting tools

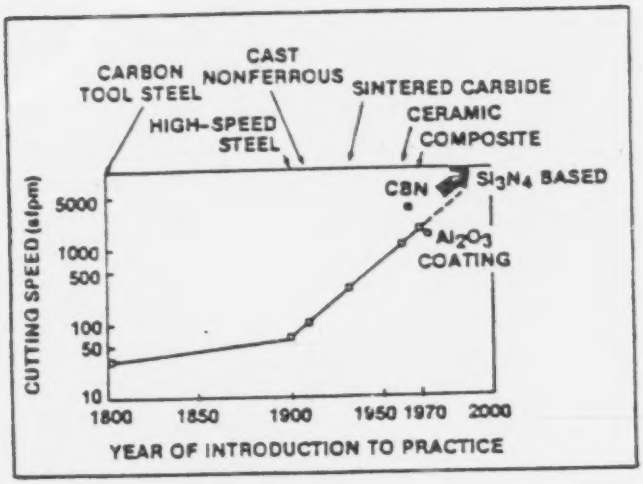


Figure 7.1. Change in productivity via the introduction of new cutting tool materials.[1]

for specific applications, because no one cutting tool is ideal for all applications. In some instances, the slower but tougher metal-based cutting tools are preferred to the faster but brittle ceramic tools.

Mechanical properties primarily determine the appropriate cutting tool material. Critical cutting tool material characteristics that determine cutting speed, tool life, and surface finish include hardness, elasticity, strength, thermal stability, and toughness. These properties are compared for cemented carbide and sintered alumina in Table 7.1. Increased hardness extends tool life, which favors ceramics. A high modulus of elasticity is also desirable since this minimizes tool deformation during cutting operations. Negative rake cutting angles compensate for the low tensile and transverse rupture strengths of ceramics by using to advantage the excellent compressive strength of ceramics. The hot hardness, high-temperature strength, and chemical inertness of ceramics give these materials a distinct advantage over the less refractory, cemented carbides. New silicon nitride cutting tools also exhibit good thermal shock resistance. Ceramic cutting tool materials lack only toughness or impact strength, and even this can be mitigated somewhat by using mixed materials or composites that possess toughening phases.

The principal features of several common cutting tool materials are illustrated in Table 7.2. Metal-based tools have the inherent advantage of toughness and thermal shock resistance. However, these tools are subject to thermal softening at the high temperatures

Table 7.1. Comparison of Physical Properties of Sintered Alumina and Cemented Carbide.[2]

Property	Cemented Carbide	Sintered Alumina
Hardness		
Microhardness (kg/mm^2)	1600	1800
Rockwell A	91-92	92-94
Melting Point (°F)	2552	3632
(°C)	1140	2000
Density (kg/m^3)	12,000-15,100	3800-3900
(g/cm^3)	12.0 - 15.1	3.8 - 3.9
Modulus of Elasticity GN/m^2 (10^6 psi)	520 - 660 (74-94)	420 (60)
Transverse Rupture Strength MN/m^2 (kpsi)	1000 - 2400 (150 - 350)	700 - 840 (100 - 120)
Compressive Strength GN/m^2 (kpsi)	4.2 - 5.6 (600 - 800)	3.9 (560)
Tensile Strength MN/m^2 (kpsi)	900 - 1000 (130 - 145)	260 (37.4)
Coefficient of Thermal Expansion Values for 25°C (77°F)	$4.5 - 7.2 \times 10^{-6}/K$ ($2.5 - 4.0 \times 10^{-6}$ in/in/°F)	$7.5 \times 10^{-6}/K$ (4.2×10^{-6} in/in/°F)
Grain Size (microns)	3	3

Table 7.2. Main Characteristics of Several Types of Cutting Tool Materials.[2]

CUTTING TOOL MATERIAL	MECHANICAL PROPERTIES (Edge Strength and Toughness)			TYPICAL CONDITIONS FOR SINGLE-POINT TURNING	
	TYPICAL TRANSVERSE RUPTURE STRENGTH GN/m^2 (kpsi)	IMPACT STRENGTH AND THERMAL SHOCK RESISTANCE	ABRASIVE WEAR RESISTANCE	RAKE ANGLES (DEGREES)	CUTTING SPEED m/sec (ft/min)
High speed steels	3.8-4.6 (550-650)	Increasing ↑	Increasing ↓	+5 to +30	0.39-0.91 (75-180)
Cast cobalt-base alloys	1.4-2.8 (200-400)			0 to +20	0.38-1.32 (75-260)
Cemented carbides	1.0-2.4 (150-350)			-6 to +10	0.76-9.14 (150-1800)
Ceramics (black)	0.84-0.94 (120-135)			-15 to -5	12.7-25.4 (2500-5000)
Ceramics (white)	0.70-0.84 (100-120)			-15 to -5	2.54-15.2+ (500-3000+)

generated by high cutting speeds. On the other hand, ceramic tools excel in wear resistance and cutting speed due to the inherent high hot hardness of ceramics, but exhibit low fracture toughness. However, Table 7.2 does not include new data for silicon nitride cutting tools, which exhibit twice the fracture toughness of alumina.[1] As these new silicon-based tool materials are developed and improved, the role of ceramics in cutting tool operations will expand significantly.

Cutting Tool Materials

Materials currently being used in cutting tool applications can be classified into four major groups: steels, cemented carbides, ceramics, and superhard materials. This range of available cutting tool materials is the result of historical usage and economics. The current trend in the development of cutting tool materials is clearly towards extremely hard materials such as ceramics and diamond, and away from tough materials like steel (Table 7.1).

High Speed Steels

High speed steels (HSS) are the traditional material used in milling, boring, drilling, and other common cutting tool operations. HSS cutting tools are generally used on soft metals where toughness is required. The major limitations of HSS tools are low cutting speeds, because of its limited temperature tolerance, and poor wear resistance.

Cemented Carbides

Blades, tips, and inserts of uncoated cobalt cemented tungsten carbide cutting tools are used to machine cast irons, non-ferrous metals, non-metallics, and some high-temperature alloys. Machining operations include roughing and finishing, milling, turning, and drilling. Cemented carbides are relatively tough and can operate at cutting speeds two to five times faster than those capable with HSS. Hot hardness is maintained up to the temperature range of 900 to 1000°C. However, cemented carbide tools are not as tough as HSS, require the use of cobalt and tungsten, which are both strategic materials, and crater at high speeds.

Ceramic Coated Cemented Carbides

Ceramic coated carbide cutting tools combine the best features of the uncoated carbide tool with the hardness, abrasion resistance, and high-temperature and chemical resistance of the ceramic coating. A chemical vapor deposition process is used to apply a high density, well-bonded alumina coating to the tool substrate. These coatings can improve wear resistance by 200 to 500% and allow high speed use, which results in higher productivity. The increase in tool wear resistance due to the ceramic coating and the high strength contributed by the cemented carbide base make this a good substitute for standard cemented carbide tools. Approximately 30% of all carbide tools are ceramic coated, thereby reducing, but not eliminating, the use of strategic materials.

Ceramics

Alumina

Ceramic cutting tools, primarily alumina-based, have been commercially available for the last 40 years. However, the inherently poor thermal shock resistance and low fracture strength of alumina-based ceramic tools (Table 7.1) have limited market penetration to less than 2%.

Ceramic tools are fabricated by two principal methods. In one, powders are milled to attain a uniform mixture and particle size distribution. The powder is then pressed to the desired configuration and sintered at high temperatures. After firing, the tool is ground and finished to final tool specifications. In the second method, the tool is hot-pressed, which involves the simultaneous application of both heat and pressure to starting powders. Hot-pressing often provides better microstructural control and higher part densities in shorter processing times. However, this process is more expensive than the first method, and limits tool geometries to standard shapes.

Improved processing techniques and a better understanding of microstructure-property relationships have led to considerable improvements in the thermal shock resistance and fracture toughness of alumina cutting tools. Small amounts of magnesium oxide added to the alumina starting powder inhibits grain growth during sintering. Small amounts of molybdenum are added to aid grain refinement, which is essential for strength. Titanium carbide inclusions strengthen the alumina matrix. The dispersion of fine carbide particles

increases the fracture energy of the inherently brittle alumina, thereby improving tool life and dependability. In addition, surface finishing techniques that minimize surface flaws on the tool further enhance its strength and impact resistance.

Sintered alumina is harder and melts at higher temperatures than cemented carbides (Table 7.1). Modulus of elasticity, compressive strengths, and microstructure can be controlled to yield properties equivalent to carbides. The major limitations of this ceramic are its low tensile strength and poor thermal shock resistance. The improper use of traditional coolant with these tools often causes thermal shock and tool failure.

Silicon Nitride

The introduction of silicon nitride (Si_3N_4) tools is the latest development in ceramic cutting tools. Newly developed Si_3N_4 materials and silicon aluminum oxynitride (sialon) have a great potential for penetrating the cemented carbide market. A summary of the properties of cemented carbide, alumina, and new Si_3N_4 tool materials is provided in Table 7.3. The advantages of these new tool materials include high hardness, high-temperature strength, thermal shock resistance, chemical inertness, and higher fracture toughness. The superior performance of these tools are illustrated in Figure 7.2.

The major advantage of these tools is the ability to run at very high cutting speeds, which increases productivity. At high cutting speeds of more than 1000 sfpm, these tools perform better than both cemented carbide and coated ceramic tools. Silicon

Table 7.3. Comparison of Tool Materials.[4]

Material	Density (g/cm³)	Thermal conductivity (W/(m·K))	Coeff. of thermal expansion, per °C (×10⁻⁶)	Hardness (Rockwell "A")	Melting point (°C)	Compressive strength (MPa)	Transverse rupture strength (MPa)	Tensile strength (MPa)	Modulus of elasticity (TPa)
Metal carbides									
C-5*	12.6	50.21	5.5	91	1400	5500	1700	950	0.58
C-8*	5.6	16.74	2.4	93	1400	4100	1400	950	.58
Pure Al_2O_3*	3.9	16.74	7.4	93.5	2000	3900	700	260	.41
Composite Al_2O_3*	4.2	20.92	7.8	94	2000	4400	800	260	.41
S-8 Si_3N_4	≈3.3	"Good"†	2.6‡	95	1750§	2800‡	690¶	NA**	NA**
Quantum 5000™	3.19††	27.00	4.0	93.5	≈1800§	NA**	830‡‡	NA**	0.28

*Data obtained from Ref. 2. †Exact data unavailable. ‡At 500°C. §Sublimation temperature. ¶Reported by Ford as "roughly four times the 'flexural strength.' " ‖Reported by Ford as "flexural strength in four-point bend test," with a potential of 1100 MPa. **NA = not available. ††Reported by GTE Precision Materials as 3.76 g/cm³ when as a composite with TiC. ‡‡Reported by GTE Precision Materials as "flexural strength in four-point loading at room temperature," as 700 MPa at 1000°C, and as 410 MPa at 1200°C.

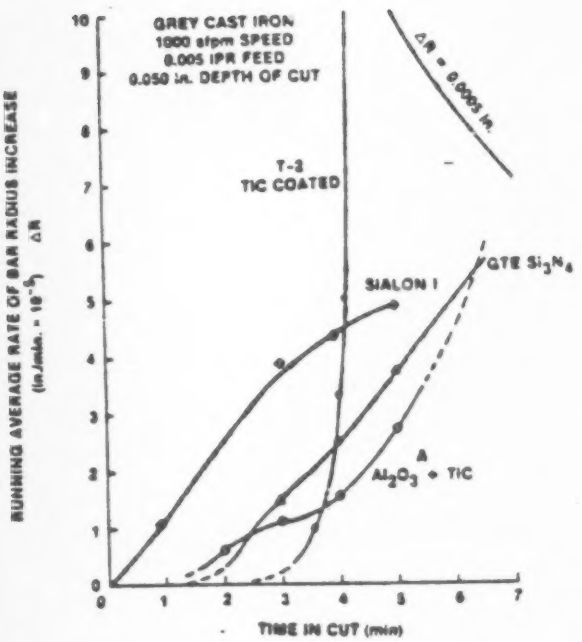


Figure 7.2. Performance of selected ceramic cutting tools in gray cast iron machining compared to TiC acoated WC-Co tool.[3]

nitride tool bits also have excellent thermal shock resistance and can be used with a coolant, although it is not required. This allows for production techniques resembling standard WC-Co tools and alleviates an existing institutional barrier.

A recent study at GTE, Inc. which is marketing a new silicon nitride cutting tool, has demonstrated that the new tool material achieved significant increases in productivity (Table 7.4). Other data on the wear resistance of these tools indicated that they outperformed standard tools in experimental testing for cast iron machining. As better microstructural control, coatings, surface treatment, and new materials such as silicon nitride and sialon are developed, ceramics should gain a significant portion of the cutting tool market. However, some problems remain. In order to operate at higher cutting speeds, greater power is required. Higher speed also induces a greater degree of vibration; too much vibration will cause a ceramic tool to shatter. Therefore, a more rigid and stable machine tool is required. High-speed ceramic tools require the costly development of new cutting tool machinery with greater power, better rigidity, and more stability. Cutting tool machinery designed for metal-based tools have insufficient power, rigidity, and speed to take full advantage of hard, wear resistance ceramic tools.

Superhard Materials

Superhard ceramic cutting tool materials include polycrystalline diamond (PCD), cubic boron nitride (CBN), and boron

Table 7.4. Field Test Results on Rough Machining of Brade Drum.[5]

Operation	Number of Parts Machined Per Index					
	1	2	4	5	6	7
Al_2O_3 Based*	10	25	20	20	25	30
Quantum 5000**	120	120	120	120	120	120

*Data Obtained from Manufacturer
**Test Stopped before Tool Failure

carbide. These materials are replacing traditional or other carbides in many nonferrous cutting applications where long tool life is essential or standard tools are not good enough. In particular, PCD provides extremely long tool life and possesses inherent toughness or resistance to shock loads. In such applications, these expensive cutting tool materials can be cost effective.

Superhard materials are expensive due to their raw material cost, processing cost and finishing costs. Finishing costs are particularly high due to the hardness of these materials. Finishing operations require expensive equipment and highly skilled labor.

Barriers to Ceramic Cutting Tool Use

In 1979, E. Dow Whitney of the University of Florida conducted a national survey of ceramic cutting tool manufacturers to define those factors constraining the application of ceramic tools in metalworking technology. Several specific problems were identified. First, consumers were reluctant to use ceramic tools because of insufficient knowledge of their properties and proper use. Inappropriate use of a coolant with ceramic tools results in failure due to thermal shock. However, the long-standing use of a coolant in machining operations is a very difficult habit to break. Also, machinists instinctively reduce cutting speed when they encounter machining problems. Ceramic cutting tools perform best at high cutting speeds; therefore, machine speeds should be maintained or increased to alleviate the problem. The few ceramic tool

manufacturers in the market at the time of the study had generated relatively little information about their product.

Second, inadequate machine tools were identified as a major problem. Many existing machines have inadequate rigidity, stability, speed, and power to take full advantage of ceramic cutting tools. In addition, machine tool users were generally not aware of the overall economics of ceramic cutting tool costs. The prospect of needing new machine tools deterred potential users before they even considered the real cost benefits of these tools in terms of higher productivity.

Whitney also noticed a general resistance to change. He placed the responsibility squarely with the ceramic tool makers to adequately advertise and market their product, providing technical assistance in the process. Improvements have been made since Whitney's 1979 survey though much remains to be done.

Market Analysis

The United States has not been the leader in the development or implementation of new ceramic cutting tools. Japan and Germany have assumed leadership in this area, as reflected by actual trade data for all tools (Table 7.5), even though most of the original research and development on the newest cutting tool materials, sialon and silicon nitride, took place in the United States.

Japan and Germany have clearly recognized the direct relationship between cutting tool speed and productivity[8] and have focussed their attention upon ceramics. In particular, Japan's

Table 7.5. Trade Data, Metal Cutting Tools.[7]

Jan. - July 1979	
U.S. Exports*	
Canada	$10.7
Mexico	3.9
United Kingdom	3.8
West Germany	3.3
France	2.3
Japan	1.7
U.S. Imports*	
Japan	$ 8.3
Sweden	6.8
West Germany	5.4
United Kingdom	4.4
Israel	4.0
Yugoslavia	3.5

Jan. - July 1980	
U.S. Exports*	
Canada	$15.3
Mexico	7.0
West Germany	5.5
United Kingdom	4.6
France	2.7
Japan	2.1
U. S. Imports*	
Japan	$13.4
West Germany	8.5
Yugoslavia	6.4
Sweden	5.8
United Kingdom	5.7
Israel	5.2

* Millions of dollars

national effort to increase productivity has encouraged the use of new ceramic cutting tools. Large, capital-intensive industries such as the automotive industry have led this effort. These companies regard powerful machine tools that are capable of very rapid machining rates essential to remaining competitive. High quality ceramic cutting tools not only favor high cutting speed, but also offer long tool life, minimizing the downtime associated with the replacement of inserts. In particular, automatic machine tools and production systems make tool reuse impractical and increase the demand for throw-away tools in place of semi-permanent ones.

The current trend towards near-net-shape technology also favors this use of ceramic tools for high-speed, light-finishing operations. Currently, 55% of all throw-away cutting tools used in Japan are cemented carbides, including the coated carbides, which is probably similar to the situation in the United States. However, the use of carbides in Japan is declining steadily, primarily as a result of the demand for higher cutting speeds. Whereas conventional alumina-based cutting tools could be used at higher cutting speeds than carbides, their application was limited due to their low fracture toughness.

The creation of new ceramic tool materials such as the Al_2O_3-TiC composite, sialons, and other silicon nitride-based ceramics[4] has given a new dimension to ceramic cutting tool technology. The major technological advance is improved fracture toughness. In addition, silicon nitride has thermal shock resistance comparable to cemented carbides and can be used with a coolant even though it is

not required. Ceramics are now used routinely in interrupted cutting operations. They have achieved the level of reliability required for use in high-speed cutting on automatic production systems such as numerically controlled machine tools. Significantly, there is a much higher percentage of new machine tools (machines less than 10-15 years old) in Japan than in the United States. Thus, in terms of overall manufacturing capability, Japan can easily take advantage of developments in ceramic cutting tool technology as they occur.[7]

The $2.25 billion U.S. cutting tool market is dominated by HSS (53%) and carbide (45%) tools. The remaining 2%, or $50 million market, consists of alumina, cermets, polycrystalline diamond, CBN, sialon, and silicon nitride tools. The applications for these materials are listed in Table 7.6.

Cemented carbide cutting tools account for only 9% of total U.S. cobalt consumption. New ceramic cutting tool materials demonstrate functional and economic viability as substitutes for carbides. As the demand for ceramic tools increases, ceramic cutting tool production economies of scale should make these tools economically competitive. However, even an optimistic near-term projection of 20% substitution of ceramic for cobalt cemented carbide cutting tools would have an impact of less than 2% on total U.S. cobalt demand.

The substitution of ceramics for conventional cutting tools will be based upon reliability, productivity, and price rather than a dependence on strategic materials, except where supply of the

Table 7.6. Ceramic Cutting Tool Materials and Uses.

Material	Use
Alumina	• turing cast iron, finishing (< 32Rc) • uninterrupted cuts on tough materials, non-metallics
Cermets	• carbon and alloy tool steels (> 32Rc) • chilled cast iron • stainless steel, Iconel, Martensite
TiN + TiC	• steels and cast iron • ferrite stainless steel, copper alloys, lead, vanadium, rubber, plastics
Sialon	• Ni-based alloys, Iconel • hard materials (> 45Rc)
Si_3N_4	• cast iron finishing
Polydiamond	• aluminum, copper, hard rubber, graphite, carbides, ceramics
Cubic Boron Nitride (CBN)	• Ni and Co superalloys • chilled cast iron, tool steels • hardened steel (50-70 Rc)

latter may affect price. In the medium-to-long term, ceramics will replace a significant portion of cobalt cemented carbide tools. This substitution will be based on productivity and economic issues. While critical material substitution is not currently a driving force for ceramic cutting tool application, it certainly could become so if supply uncertainties were to lead to cobalt price escalations.

REFERENCES

1. Buljan, S.T., and Sarin, V.K., "Silicon Nitride Compositions for Cutting Tool Application," GTE Laboratories, Inc., Profile, Waltham, MA, June 1982.

2. Whitney, E.D., "Progress in the Development of Modern Ceramic Cutting Tool Materials," SAE 810319, Warrendale, PA, 1981.

3. Buljan, S.T., and Sarin, V.K., "Improved Productivity through Application of Silicon Nitride Cutting Tools," Carbide and Tool Journal, May-June, 1982: 40.

4. Robb, S., "Ford, GTE Announce Si_3N_4 Cutting-Tool Developments," Bull. Amer. Ceramics Society, Vol. 62, No.2, Feb. 1983: 206.

5. Buljan, S.T., and Sarin, V.K., "Advanced Silicon Nitride Based Ceramic for Cutting Tools," First International Material Removal Conference, MR83-189 SME, Dearborn MI, 1983.

6. Personal communication, Corning.

7. Whitney, E.D., "Progress in Ceramics Research for Cutting Tools in the U.S., West Germany, Japan, and Sweden," Draft report, Department of Materials Science and Engineering, University of Florida, Gainesville, FL.

8. North, B., "Substitution of Ceramics for Conventional Cutting Tools," Kennametal, Inc., Draft, Greensburg, PA, 1983.

8. HEAT EXCHANGERS

Introduction

The rising cost of energy, the reduced availability of high grade fuels, and competitive pressure in high temperature industrial processes have led to the development and expanded use of energy conservation devices and equipment modifications such as high-temperature heat exchangers and recuperators. Heat exchangers and recuperators allow a furnace to operate more efficiently by using its waste heat to preheat incoming combustion air. This method of preheating combustion air directly reduces fuel consumption, with an added indirect savings derived from waste heat utilization.

Heat exchangers have predominantly been constructed from austenitic and ferrite stainless steels and superalloys that limit the preheat air temperatures possible.[1] Austenitic stainless steels can be used to a maximum temperature of about 815°C. Ferritic stainless steels can be used to a maximum temperature of approximately 700°C,[2] and are generally specified for their high oxidation resistance. Superalloys are also used in heat exchangers and have a maximum operating temperature approaching 1100°C. Table 8.1 provides a list of oxidation and sulfidation resistent heat exchanger alloys and their nominal chromium concentration. Ceramic heat exchangers outperform metallic versions in terms of both high temperature performance and corrosion/oxidation limitations. The main constraint to the expanded use of these heat exchangers is the reliability and thermal shock resistance of the ceramic tubes.

Table 8.1. Oxidation and Sulfidation Resistant Alloy Selection.[5]

Variety	Alloy	Producer	Recommended Test Temperature (°F)	Nominal Cr Concentration (%)	Other Key Elements
Austenitic Stainless Steels (Iron-Base)	321*	Republic Steel	1200 & 1500°F	18	0.35 Ti 1.0 Si
	310*	Republic Steel	1200 & 1500°F	25	1.0 Si
	20-Cb	Carpenter Technology	1200 & 1500°F	20	0.5 (Cb+Ta) 1.0 Si
	SA nicro 28	Sandvick Steel	1200 & 1500°F	28	1.0 Si
Nickel Base Heat-Resistant Alloys	Incoloy 825	Huntington Alloys (INCO)	1500 & 1700°F	22	0.9 Ti 0.3 Si 0.1 Al
	Inconel 625*	Huntington Alloys (INCO)	1500 & 1700°F	22	0.2 Al 0.3 Si 3.6 (Cb+Ta)
	Hastelloy X*	Cabot Corp.	1500 & 1700°F	22	Trace Rare Earths (?)
*Prior Solar experience in recuperators or heat exchangers					

Variety	Alloy	Producer	Recommended Test Temperature (°F)	Nominal Cr Concentration (%)	Other Key Elements (% Wt)				
					Fe	Mo	Cb+Ta	Al	Ti
Nickel-Base Heat-Resistant Alloys	Inconel 671 (Cladding on Incoloy 800H Base Tube) (Ref. 13)	Huntington Alloys (INCO)	1500°F 1700°F 2000°F	48	—	—	—	—	0.35
	Inconel 690	Huntington Alloys (INCO)	1500°F 1700°F 2000°F	30	9	—	—	—	—
	Incoloy 825	Huntington Alloys (INCO)	1500°F 1700°F	22	30	3.0	—	0.1	0.9
Austenitic Stainless Steel (Iron-Base)	SA nicro 28	Sandvik Steel	1200°F 1500°F	28	Bal	3.5	—	—	—
	20-Cb	Carpenter Technology	1200°F 1500°F	20	Bal	2.5	0.5	—	—

The major driving force for the development and use of ceramic heat exchangers is their higher temperature capability. Ceramic heat exchangers can can be used to 1200-1600°C, thus increasing the preheat air temperature by at least 400°C. Studies have shown that for every 140°C increase in combustion air temperature there is approximately a 5% reduction in fuel consumption. Therefore, a minimum fuel savings of 15% is possible, and actual studies have indicated even greater fuel savings of 30-60%.[3] The other major benefit of ceramic heat exchangers is oxidation and corrosion resistance which provides a longer component lifecycle and improved operating efficiency of the unit.

Heat Exchanger Design and Materials

Heat exchanger designs vary with the application. However, there are three basic designs for energy transfer between hot waste gases from the stack and cool, incoming air. These include counter flow, parallel flow, and cross flow and are illustrated in Figure 8.1. The heat transfer is accomplished by either convection or radiation. Metal recuperators using a parallel flow design, radiation heat transfer, and cooling can operate at temperatures above the alloy's use temperature at approximately 1000°C. Lower temperature recuperators, using convection heat transfer and usually a cross flow design, are limited to about 980°C because of the rapid deterioration of the metallic alloys at high temperatures.[4]

The ceramic materials which may replace alloys in heat exchangers include silicon carbide (SiC), silicon nitride (Si_3N_4),

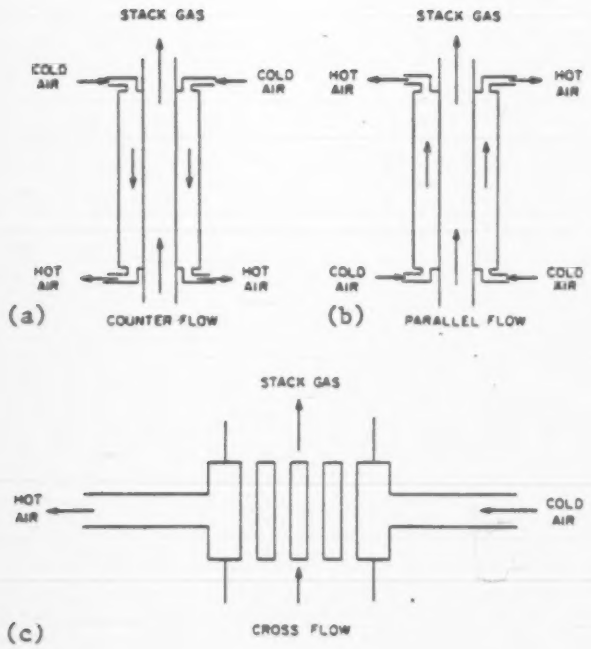


Figure 8.1. Three types of gas flow paths used in recuperators.

aluminum oxide (Al_2O_3), lithium aluminum silicate (LAS), and cordierite (MAS or $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$). Most major industrial recuperation development programs have focussed on SiC, which is used in heat exchangers for gas turbine power generation, coal gasification, co-generation, and for aluminum remelting, glass-melting, and steel soaking pit furnaces. LAS has also been used as a regenerator/heat exchanger in the gas turbine engine. Small recuperators, designed for use on a single gas or oil fired burner, use MAS. Experiments with Al_2O_3, which is susceptible to corrosive attack, and Si_3N_4, which has a low oxidation resistance, have been less successful. Some composites and glass/ceramics have also been developed which incorporate a honeycombed structure into the heat exchanger design.

Applications

Power generation units are an important application of heat exchangers. A major difficulty in the design of heat exchangers for power generation systems is tube-to-tube and tube-to-header attachment. A relaxing joint resolves this problem somewhat by joining two ceramic tubes together with a glass filler. In addition, regulating thermal conditions can control this joint to attain a minimum of permeability. Tests indicate that the joint can be maintained for at least 100 hrs at 704°C and 689 kPa (100 psia) internal pressure without significant leakage. Airtight ceramic-to-ceramic spherical joints are another solution to the attachment problem. These joints are braized with a developmental alloy that

can withstand 704°C, 551 kPa, and an end load of 20 kgm for 25 hrs without leakage.[6] Figure 8.2 provides a schematic diagram of this heat exchanger configuration. A similar heat exchanger in a coal-fired gas turbine, power generation system is shown in Figure 8.3.

The Gas Research Institute (GRI) has conducted studies on the use of heat exchanger/recuperators in glassmelting, aluminum remelting, and steel soaking pit furnaces. The primary focus of these studies was to develop a material base that could withstand the corrosive environment present in each of these applications and would allow the use of waste heat to preheat the combustion air. This would reduce fuel consumption and create higher energy efficiency, making natural gas competitive with other fuel sources in these furnace applications. The principle materials analyzed were SiC, siliconized SiC, and chemical vapor deposited SiC (CVD-SiC). New heat exchanger designs including new tube-to-header joining technology were developed.

The GRI also made an effort to develop low cost ceramic tubing for use in heat exchangers. These tubes are made by casting, extrusion, or CVD processes. Extrusion processes produce tubes with external fins and in spiral configurations, while casting produces tubes with radial fins. Before final firing, these greenware tubes are diamond ground and machined for dimensional control. The geometries of tubes produced from CVD-SiC are limited by the substrate material. Tubes can be produced with diameters up to 20cm (8in) and lengths up to 244cm (8ft). Longer lengths are less

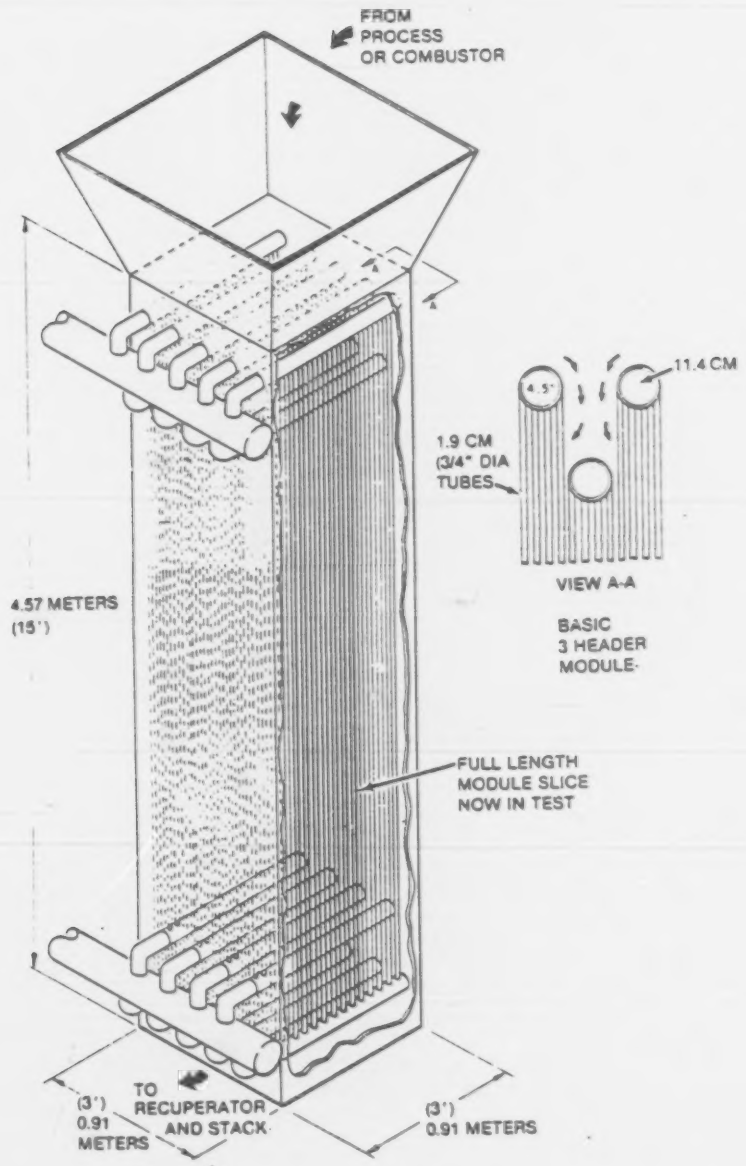


Figure 8.2. Axial counterflow heat exchanger concept.[6]

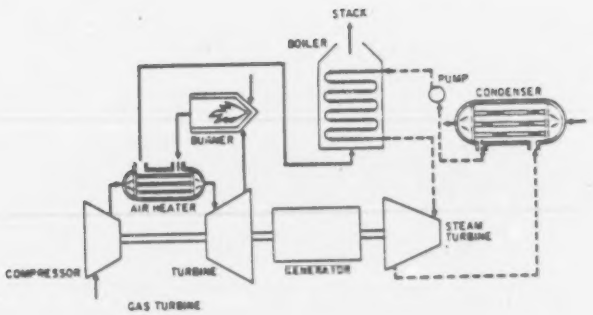


Figure 8.3. Indirect exhaust coal-fired combined cycle.[6]

readily available. However, a heat exchanger has been developed with 450cm (15ft) ceramic tubing.[5]

Economies

The properties of heat exchanger/recuperator materials and prices for various size tubes are given in Table 8.2. The price of cast and extruded tubes appear to be independent of supplier and fabrication techniques. Limited production quantities of medium length tubes of less than 2.5 m and 4 cm diameter cost $330 to $500/m. These costs drop to $165 to $230/m for production volumes on the order of hundreds per year. Producer estimates indicate that if the demand for ceramic heat exchanger tubes were to increase to volumes in the range of millions of tubes per year, the price could be reduced to $33-$66/m ($10-20/ft.). CVD-SiC is much higher in price due to the long processing time required to build up an adequate reaction layer on the graphite foam substructure. Major cost reductions through mass production of these tubes are a realistic expectation. Past experience in the fabrication of ceramic honeycomb structures for automobile catalytic converters reduced costs from $8.0/in^3 to $0.25/in^3 for the high volumes required by the automotive industry.[5]

DOE and GTE have funded the design of a small MAS recuperator for use with individual burners. The size of these recuperators alleviates the space constraint associated with small furnaces. They are particularly useful for furnaces that are an integral part of a larger manufacturing process such as forge reheating, heat-

Table 8.2. Properties and Prices of Selected Ceramic Materials.

Material Name Supplier		304 Stainless Steel	KT SiC Carborundum	Sint-α SiC Carborundum	SC-2 SiC Coors	99.8% Al_2O_3 Coors	Si-Coated Graphite Midland	CVD SiC Midland	Crystar SiC Norton	NC 430 SiC Norton	Refel SiC Pure Carbon
Specific Gravity		8.02	3.10	3.16	3.10	3.82	1.85	3.22	3.10	3.09	3.10
Modulus of elasticity,	GPa	193	386	401	395	345	14	234	207	372	396
	Mpsi	28	56	58.2	57.3	50	2	34	30	54	57.5
Tensile Strength,	MPa	572	142	-	307	∿ 269	14	172	-		310
	kpsi	83	20.6	-	44.5	∿ 39	2	25	-		45
Compressive Strength,	MPa	572	1034	3895	2482	<2068	83	820	689	1723	3447
	kpsi	83	150	565	360	< 300	12	119	100	250	500
Flexural Strength,	MPa	-	157	459	517	331	190	689	300	303	517
	kpsi	-	22.8	66.6	75	48	27.6	100	43.5	44	75
(# points, @ °C)			(MOR,25)	(4 pt,25)	(3 pt,25)	(3 pt,25)	NA	NA	(MOR, 25)	(MOR, 25)	(3 pt,25)
Poissons Ratio		0.3	NS	0.14	0.19	0.22	NA	NA	NS	NA	0.24
Hardness		240 Brinell	2200 Knoop, 20 gm	2800 Knoop, 100 gm	1950 Knoop, 200 gm	∿ 2000 Knoop, 1000 gm	NA	NA	2700 Knoop, 100 gm	1650 Knoop, 200 gm	1974 Knoop, 200 gm
Coefficient of Thermal Expansion, $°C^{-1}$ (at °C) x 10^{-6}		17	4.7 (20-980)	4.0 (25-700)	4.3 (25-1000)	8.0 (25-100)	4.3	4.5 (25-1000)	4.8 (25-1500)	4.9 (?)	4.3 (20-1000)
Thermal Conductivity, w/m°K		16.3	86	∿ 50	83.6	∿14.5	52.1	39	26	50	86.9
(@ °C)		(100)	(25)	(600)	(500)	(100)	(?)	(600)	(540)	(650)	(400)
Porosity, %		0	0	0	0	0	0	0	15	0	0
Maximum Useful Temperature, °C		800	1300	1300	1300	1800	NA	1350	1400	1300	1300
Cost											
In Limited Production											
$/M @ Dia		-	328-492@4cm	328-492@4cm	410@4cm	-	492@4cm	1640@4cm	∿ 328@4cm	328@4+8cm	328-492@4-8cm
$/ft @ Dia		-	100-150 @1"	100-150@1"	125@1"	-	150@1"	500@1"	∿ 100@1"	100@1"+2"	100-150@1"+2"
In Hi-Quantity											
$/M @ Dia		16@4cm	16-33@4cm	16-33@4cm	46@4cm	-	16@4cm	197@4cm	NA	33-66@8cm	NA
$/ft @ Dia		5@1"	5-10@1"	5-10@1"	14@1"	-	5@1"	60@1"	NA	10-20@2"	NA
					∿ 16@4cm*					19-23@4cm	
					∿ 5@1"*					6-7@4cm	
Corrosion/Oxidation Resistance in 1000°C Coal Environment		Fair	Good	Good	Good	Poor	Poor on Graphite, Good on SiC	Excellent	Good	Good	Good

treating, ladle heating, thermal reduction, calcining, and slab and box forges. Battelle Columbus Laboratories (under a DOE contract) analyzed furnace operating cost before and after these recuperators were installed. Based on the analyses of a oil-fired box forge furnace, fuel savings of 50% were realized. Payback periods for the entire system were approximately 1.33 years, based on fuel savings at $1.30/gallon fuel cost.[8]

Another recuperator, designed for small-to-medium furnaces, incorporates a ceramic matrix into a cross-flow recuperator design. Previous metallic designs were temperature (800° C) and corrosion (SO_3) limited. The ceramic recuperator uses cordierite (MAS) in a triple, air-pass, layered construction. The maximum operating temperature is 1375°C, more than 600°C higher than that of the metallic system. The MAS recuperator also has good corrosion resistance and excellent thermal shock resistance. In addition, the most effective metallic recuperator can generate only a 20% to 30% fuel savings. However, with the increased temperature capability of the ceramic recuperator, fuel savings of 50% or more are possible.[8]

Much of the present burner technology is based on high-temperature stainless steels and alloys. These burners have the same temperature limitations as metallic recuperators. Consequently, there is the increasing need to develop higher temperature refractory burners to take advantage of the higher combustion air temperature being delivered by ceramic-based recuperators. Ceramic tubes are now used as flame stabilizers in newly developed burners, thereby increasing the operating

temperature capability. Refractory nozzles will also replace those of stainless steel in these high temperature burners.

The economic benefit, in terms of energy efficiency, for adding a recuperator to a previously unrecuperated furnace can be as large as 40 to 50% fuel savings. While the first-of-a-kind cost of such a system is high, the estimated cost of subsequent systems is very encouraging (Table 8.3), assuming large production volumes and economies of scale. The payback period for this high-temperature, burner duct recuperator for a steel soaking pit furnace is approximately two years, assuming at least a 50% cost reduction in ceramic tubing. At present, ceramic tubing accounts for roughly 25% of the total cost of the heat exchanger. Estimates indicate that in order for the process to be economically reliable, ceramic tubing costs must be reduced to 20% of their current cost. This appears to be possible, based on producer estimates presented in Table 8.2.

Summary

Ceramic heat exchangers and recuperators are both technically and economically substitutable for state-of-the-art metal recuperators in many applications. Although it is difficult to determine the actual tonnage of the metal replaced, ceramics replace metal alloys which contain high percentages of chromium (18%-25% by weight), small amounts of manganese (approximately 2%), and occasionally cobalt (about 10%). However, substitution for these materials is not the primary driving force for the use of ceramics in these applications. Ceramics will be used because of their high-

Table 8.3. System Fabrication and Installation Expense.[7]

Item	Current First-of-a-Kind Costs ($x10^3$)	Estimated Costs With Quantity Purchasing and Other Reductions ($x10^3$)
1. Burner	33	10
2. Burner Controls	7	5
3. Ceramic Sleeves & Seals	27	20
4. Ceramic Tubes	251	125
5. Combustion Air Fan	15	15
6. Dampers	20	5
7. Ducts	6	3
8. Emergency Cooling System	4	4
9. Fabrication	55	40
10. Induced Draft Fan	10	10
11. Installation	50	50
12. Installation Materials	30	15
13. Insulation	15	15
14. Process Controls	150	30
15. Steel	9	9
SUBTOTAL	*682	356
G&A, Profit (35%)	---	125
TOTAL	682	*481

- - - - -

*Add $25K for a metallic recuperator for use in an unrecuperated furnace

temperature performance, potentially low cost, and subsequent overall economic advantage.

Ceramics do appear to perform better than several superalloys in highly corrosive environments. Ceramic materials also allow maximum operating temperature capabilities to be increased by approximately 600°C. An industry rule-of-thumb indicates that this will yield an approximate 50% reduction in fuel consumption due to this high-temperature combustion air. Enhanced corrosion resistance may result in longer component lifetimes, although the effect of higher temperatures on furnace and refractory lifetimes has not yet been fully quantified.

At the present state of technology, large-scale heat exchangers and recuperators based on SiC tubes are not economically viable. The cost of the SiC tubes represents approximately 25% of the cost of the system. Estimates indicate that this cost must be reduced to 20% of its present value to be economically viable. Several programs are in progress to reduce the cost of these tubes and have been somewhat successful. Significant advances have already been made in ceramic/ceramic and ceramic/metal joining technology.

Small, single burner recuperators based on MAS for unrecuperated small furnaces are now economically viable. These units have been installed in 41 different industrial furnaces in a DOE funded test program, and have demonstrated fuel savings of 40% to 60%. The current market for this type of recuperator is approximately $250 million. Approximately 50% of this market may

install ceramic recuperators in the next five years, depending upon economic conditions and energy prices.

Future use of ceramic materials in heat exchangers and recuperators will be driven by unit cost, economic conditions, and energy costs. The performance advantage of ceramics in recuperation systems will encourage their use in new and unrecuperated furnaces. A changeover from systems currently using metal recuperators will be slow due to high investment cost for large scale industrial furnace installations. However, such an energy efficient investment cannot be overlooked for long in today's increasingly competitive economy.

REFERENCES

1. Russell, A.D., Smeltzer, C.E., and Ward, M.E., "Waste heat Recuperation for Alumimium Furnaces," Solar Tubines Inc., Gas Research Institute, GRI 5081-342-0493 SR82-R-5015-13, April 1983.

2. Tennery, V.J., "Economic Application, Design Analysis, and Material Availability for Ceramic Heat Exchangers," Oak Ridge National Laboratory, Fossil Energy Program, ORNL/TM-7580, January 1981.

3. Kohnken, K.H., "Are Ceramics Better Than Metal for High Heat Recuperation," Heat Treating, Feb. 1982.

4. Tennery, V.J., and Wei, G.C., "Recuperator Materials Technology Assessment," Oak Ridge National Laboratory, ORNL/TM-6227, February 1978.

5. McFarlin, D.J., Sgamboti, C.T., and Lessard, R.D., "Ceramic Heat Exchanger Applications Study," United Technologies Research Center, subcontract 86X-92352, DOE No. W-7405 eng. 26, Oct. 1982.

6. Ward, M.E., Metcalfe, A.G., and Dapkunas, S.J., "Ceramic Tube Heat Exchanger Technology Development for Indirect-Fired Gas Turbine Cycle," Journal of Engineering for Power, Vol. 105 (April 1983): 310-316.

7. Snyder, J.E., "High Temperature Burner-Duct-Recuperator System Evaluation, System Economic Performance Analysis, Subtask 2.5," Babcock and Wilcox Company, DOE DE-FC07-81ID12296, March 1983.

8. Kohnken, K.H., "Heat Recovery Technology saves 50% in Fuel," Precision Metal, May 1983, pg. 41.

9. WEAR-RESISTANT APPLICATIONS

Introduction

Near-term uses of advanced ceramic materials in wear-resistant applications include seals, nozzles, and bearings. Alumina has been used for both nozzles and seals, but does not provide the high performance characteristics necessary to replace tungsten carbide-cobalt (WC-Co) seals. Newly developed silicon (Si)-based ceramics can compete favorably with WC-Co seals in high performance applications which require thermal stability and wear resistance. Refractory nozzles for high-temperature, heavy corrosion environments are being manufactured from Si-based ceramics. Lightweight, low-friction bearings for high-speed, high-temperature systems may become cost competitive with existing technologies.

Seals

Ceramics are used as seal rings and faces in high performance applications. Recent updates of the American Petroleum Institute pump industry Standard (API-610) specify silicon carbide (SiC) as a seal material.[1] Pump seals in the chemical processing and petroleum refining industries must be highly resistant to wear. The hardness, specific weight, strength, and thermal expansion of SiC seals all compare favorably with competing materials (Figure 9.1).[2]

Silicon carbide seals, which have greater wear-resistance than WC-Co (Figure 9.1), can be used alone or in conjunction with WC-Co. Tribological properties of SiC make it an ideal choice in highly

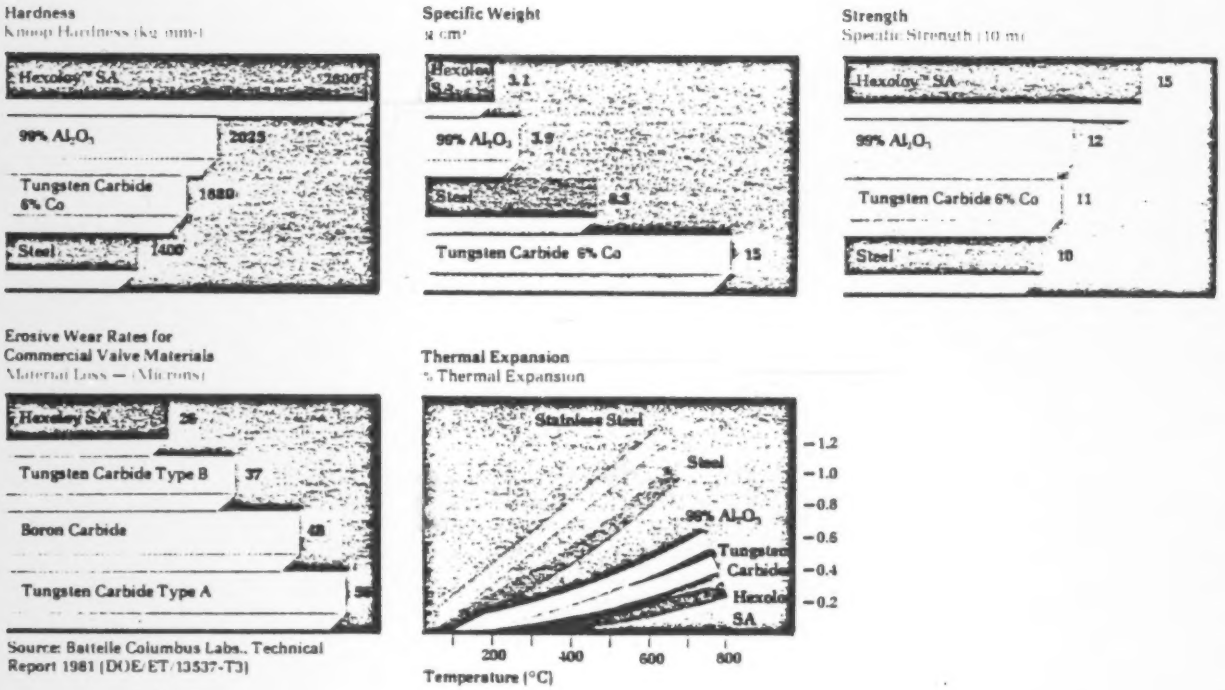


Figure 9.1. Properties of silicon carbide (Hexoloy™) and the materials for which it can substitute in seal applications.[2]

abrasive applications where two hard materials rub against each other. However, SiC is brittle, and SiC seals require diamond machining and careful handling to avoid chips and cracks. Large sizes (more than 8 inches diameter) are more expensive than competing materials. Large-sized SiC seals cost more because of the inherent difficulty of manufacturing a large part (greater probability of a critical flaw) and added finishing costs. The variation in ceramics materials supplied by different manufacturers can also be a problem for seal manufacturers, who have been reluctant to accept the use of ceramics in seals.

To date, the materials used in seals are reaction-bonded SiC, which contains free silicon metal, and sintered SiC (99%). Ceramic seal materials are hydrostatically pressed into tubes which are then sintered or reaction-bonded. Green-machining may be performed on the tubes before they are sintered to final densities. Diamond machining is used to slice the tubes into seal components which are then ground to final specifications. Even though diamond machining is expensive, this method can economically produce small seals (less than 6 inches in diameter). The average cost of a SiC seal is 60% of the cost of a comparable WC-Co seal. As the seal size increases, production volumes decrease due to a lower demand and production costs increase; therefore, ceramic seals become less economical.

The cost of ceramic seals has decreased significantly over the last ten years. When near-net shape processing techniques become a reality, thus reducing the amount of necessary diamond machining, the cost of ceramic seals will be further reduced. Alumina is used

as a standard seal material, and newly developed Al_2O_3-ZrO_2 toughened seals are being marketed in Germany. Silicon carbide has been the major material used for high performance seals, but Si_3N_4 and sialons have similar properties and may gain future acceptance. Improved ceramic materials properties and standardization of ceramic materials properties from different manufacturers are still required.

The current U.S. market for pump seals is approximately $100 million. The total free world market is three to four times larger. Current domestic use of SiC seals is about 20% of the domestic market, representing 100,000 - 500,000 parts per year.[1] The potential for ceramics in pump seals is thought to be around 80% of the total domestic market. This would eliminate approximately 30 tons of the cobalt used in cemented carbides for pump seal use.

The potential for increased ceramic usage in this market is large. Ceramics have demonstrated both performance and cost benefits. Materials and manufacturing development are still required; however, this is an active area of substitution.

Nozzles

Ceramics have traditionally been used in nozzle application, particularly in a number of high-temperature, highly corrosive environments. High-temperature burners require the refractoriness of a ceramic nozzle, such as one made from aluminum oxide. Zirconia is the standard nozzle used in steel production. Newer uses focus on ceramic nozzles for use in abrasive and corrosive environments.

Sand blast nozzles made from ceramics can replace a combination of Cr-Co and stellite nozzles. Alumina does not have the high performance properties achievable with the harder, covalently-bonded materials, SiC and potentially Si_3N_4 or sialon, which can provide abrasion resistance equal to Co-cemented WC.

Corrosive liquids can be pumped through ceramic nozzles, replacing Co-WC or stainless steel nozzles. Advanced ceramics provide better wear resistance than stainless steel, although they are higher in price than stainless nozzles. This is not due to raw materials cost, but to manufacturing cost. High performance performance ceramics nozzles are approximately equal to Co-WC and are 60-80% of the cost of a comparable Co-WC nozzle.

Poor impact resistance and brittleness are not generally a problem for this application. There is no hydraulic stress placed on the nozzle during use and, therefore, no problems with concentrated tensile stresses arise. The difference in using a ceramic nozzle in place of a metal is that the ceramic (especially in large nozzles) is more fragile. Additional care must be taken during transport and installations to make use of the superior ceramic properties.

A segment of the nozzle market, sand blast nozzles for construction maintenance, is a promising area for ceramic substitution. Currently, hand held sand blasters with ceramic nozzles are being produced. This is a $6 million dollar market, and ceramics outperform the previous metal nozzles. The ceramic nozzle is 20% of the weight and is cheaper, both in terms of material cost

and lifetime.[2] This use would replace a negligible quantity of Co-Cr; however, it does demonstrate the feasibility of ceramics to replace stellite, stainless steel, or other specialty metal nozzles in many industrial applications.

Bearings

Ceramics provide lightweight, low-friction bearings for high-speed, high-temperature systems. Property requirements for bearings vary with the application. Ceramics are well suited to ball and roll bearings in turbine machinery. A comparison of hardness versus wear resistance is illustrated in Figure 9.2. With two to three times the hardness of typical bearing steels, Si_3N_4 can be used to temperatures as high as 1200°C, with solid lubricants used to increase the wear resistance. At these high temperatures, standard steels and liquid lubricants can not be used. The low density of Si_3N_4 bearing allows longer fatique life due to decreased centrifugal forces generated by the orbital velocity.[3]

The current domestic market for bearings represents more than $2.5 billion.[4] These applications represent only a small fraction of the total market (less than 5%). However, a reduction in the current cost and the superior tribological properties of ceramic bearings would expand their use to a great number of applications.

A comparison of materials, relative cost, and properties suggested for bearing applications are listed in Table 9.1. The prices quoted are 1981 dollars; however, Si_3N_4 powders have decreased from around $150/kg to as low as $30/kg. Future

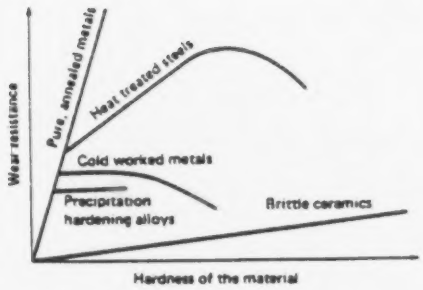
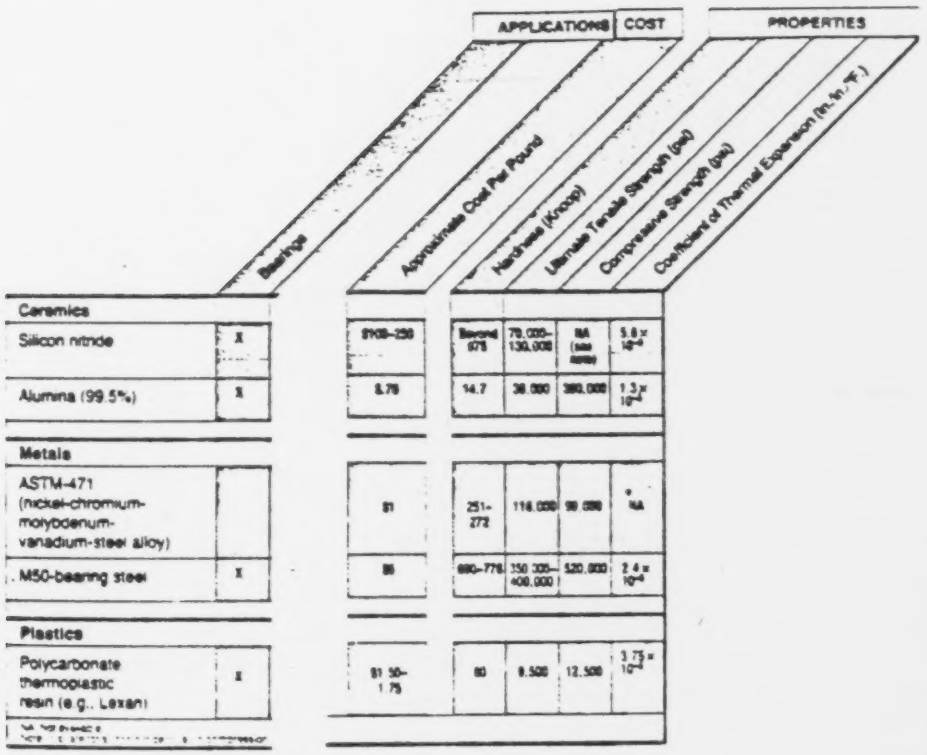


Figure 9.2. Wear versus hardness for several classes of material.[6]

Table 9.1. Ceramics and Their Competitors: Application Comparisons.[7]



	APPLICATIONS: Bearings	COST: Approximate Cost Per Pound	PROPERTIES: Hardness (Knoop)	Ultimate Tensile Strength (psi)	Compressive Strength (psi)	Coefficient of Thermal Expansion (in./in./°F)
Ceramics						
Silicon nitride	X	$100–250	Beyond 875	70,000–130,000	NA (see note)	5.0×10^{-6}
Alumina (99.5%)	X	5.70	14.7	38,000	380,000	1.3×10^{-6}
Metals						
ASTM-471 (nickel-chromium-molybdenum-vanadium-steel alloy)		51	251–272	116,000	90,000	* NA
M50-bearing steel	X	86	690–776	350,000–400,000	520,000	2.4×10^{-6}
Plastics						
Polycarbonate thermoplastic resin (e.g., Lexan)	X	$1.50–1.75	80	8,500	12,500	3.75×10^{-5}

developments in powder processing should reduce the cost to a competitive level (to as low as $5/kg)[5].

The current price of a ceramic ball for bearing applications is over $100; this is hardly competitive with M50 steel ($1-$3.50/ball). The high cost of the current ceramic bearing is due to the processing technique. Si_3N_4 powders are hot pressed into billets, then sliced and ground into balls. Due to the hardness of the material, expensive diamond machining must be used to attain the desired specifications. The cutting, grinding, lapping, and polishing process requires costly equipment and long production times, further increasing the cost. New near-net shape processing techniques (eg. cladless, hot isostatic pressing, and others) have been suggested for the formation of ball bearings. One company claims to have succeeded in producing a relatively inexpensive bearing product; however, commercial marketing is not yet a reality.

Ceramic bearings will be used in the future for high speed, high-temperature applications. Current efforts to reduce the processing cost have been successful. Research into improved materials properties have produced high quality Si_3N_4 powders that can more than compete with steel bearing on a performance scale. As the technology evolves, a competitively priced ball bearing, taking account of longer life and overall performance, should become commercially available.

Other Uses

Other near-term uses for advanced ceramics include thread guides, valves, pump parts, and crucibles. Although ceramics do not have the same ductility as the metals they replace, high performance ceramics are widely used in applications where good impact resistance and high fracture toughness is not a major requirement. These materials can be used at high temperatures and provide better wear resistance, therefore increasing performance and lifetime.

In terms of actual raw materials cost, the ceramic is often cheaper than a metal part. However, the current manufacturing technology often makes a ceramic component more expensive. As the demand for ceramic components increases, manufacturing costs will be reduced. At the present time, estimates show that economical production of ceramic parts by injection molding requires a volume of at least 1000 pieces/year. Dry pressing operations require 300-1500 pieces/year depending upon the size of the piece and the required tolerances. Slip cast parts have little volume requirement. Mold coast are low and easily fabricated to accommodate intricate shapes. However, the properties generated through this technique (density, strength, and toughness) are not as good as those produced by other methods. Hot pressing, which often yields the 'best' properties, requires expensive diamond machining and is limited to simple shapes.

Other factors also influence the use of ceramics in existing markets. In some instances, such as pump linings for corrosive liquids, ceramics provide a much longer service life for the pump.

However, one industry source claims that the manufacturers of these pumps base their sales price on a replacement parts market. The pump is priced competitively and the linings are replaced frequently. A lining with a longer service life would not be a particularly attractive application from the pump manufacturers standpoint. The handling of ceramic parts also requires significantly more care than metals. These are examples of industry and institutional barriers that must be overcome before ceramics will gain widespread use.

The technical feasibility of advanced ceramics in a number of applications has been demonstrated. The extent to which ceramics will penetrate these markets will be strongly affected by performance/cost tradeoffs. Progress has been made in both materials development and manufacturing technologies. The future of these applications will depend upon the continued evolution of the technology and the reduction in processing cost.

References

1. Griener, H., EG&G Sealab, Personal Communication, August 1983.

2. "Hexology", High Performance Engineered Silicon Carbide," Design Brochure, Carborundum, 1982.

3. Torti, M.L., "Processing Hot Pressed Silicon Nitride for Improved Reliability: HS-110 to NC-132," ed. Lenoe, E.M., Katz, R.N., and Burke, J.J. (Plenum Publishing Corp, 1983).

4. Johnson, L.R., Teotia, A.P.S., and Hill, L.G., "A Structural Ceramics Research Program: A Preliminary Economics Analysis," Report, Center for Transportation Research, Energy and Environmental Systems Divisions, ANL/CNSV-38, 1983.

5. Bowen, H.K., "Technology Base for Japan's Ceramic Thrust," Unpublished Draft, M.I.T., August 1983.

6. "Properties and Selections: Stainless Steels, Tool Materials, and Speical-Purpose Metals," Metals Handbook, 9th ed., vol.3 (Metals Park, OH:American Society for Metals, 1980).

7. McDermott, J., "Ceramics," Technology, Nov-Dec (1981): 19-30.

10. NONDESTRUCTIVE EVALUATION OF CERAMICS

Introduction

The use of ceramics in high technology applications is limited by their reproducibility and reliability. Failure in ceramic components is due to cracks, solid inclusions, voids, and other processing flaws. Nondestructive evaluation (NDE) techniques are being developed to detect these flaws and to determine their size, shape, concentration, and type. Determination of the severity of the flaw population in a component can be used to predict failure and lifetimes. An accurate data base needs to be developed to relate flaw type and distribution to mechanical properties (strength and toughness) in order to develop consistent criteria for accept/reject decisions.

A summary of the currently available NDE techniques and their limitations follows.

NDE Measurement Techniques

Ultrasonic Methods

Automated ultrasonic NDE techniques use a focussed transducer to detect flaws. The transducer is rastered across the component, and power scattering by a pulse echo technique is used to map the defects dimensions and position in three-dimensional space.[1] Components for testing are usually submersed in a water bath. The water provides transmission/acoustic coupling, but does present problems. Water limits the attenuation by limiting the frequency. Since most ceramics have a high elastic modulus (MOE) and test

specimens are small, the acoustic waves travel very rapidly through the specimen. The MOE and geometry of the specimen severely limit resolution of the defect and the sensitivity of the measurement. Ultrasonic measurements also require parallel surfaces for measurement, limiting test specimens to simple geometries.

The advantages of ultrasonics provide the ability to detect small inclusions (~50μm), higher resolution, and better locational accuracy than radiographic techniques for the determination of flaws in the bulk of the material. The disadvantages are that the defect type can not be determined, cracks near the surface are not detectable (the specimen must be examined from both sides),[2] and it is difficult to attain any degree of resolution and sensitivity in porous materials. Another factor for consideration is the long time required and limitaions of the specimen geometry for even automated ultrasonic scanning making this technique difficult to implement on a production scale.

Advances are being made in ultrasonic NDE. High frequencies (200 MHz) are being used to attain information on defect size, type, and shape. Direct methods of transducer/component contact may reduce the resolution limits imposed by the water bath. This method could overcome complex shape and near-surface problems by providing a match between acoustic impedance and wave velocity. Finally, surface wave ultrasonic techniques are being developed to detect small surface cracks in complex geometries. None of these techniques is currently advanced enough to provide an accurate NDE on a commercial scale.

Radiography

X-Radiography. X-radiography uses an X-ray beam to illuminate one side of the test object and records the resulting transmitted beam on the other side.[1] Flaw detection is characterized by changes in the intensity of the transmitted beam. This technique is well developed and automated. Flaws in the bulk or volume of the specimen can be determined with this technique; however, there are several limitations.

Microfocus x-ray with image enhancement can detect small flaws (~25μm) of high density material, however, there must be a significant difference between the atomic number of the flaw and the matrix. Resolution is severely limited by image contrast. The image contrast is determined by the test object's density, thickness, atomic number, differential x-ray absorption coefficient and the energy of the illuminating x-ray. Therefore, detection is most accurate with flaws that differ substantially from the matrix. The ability to locate the defect in three-dimensional space is also limited. This has been somewhat improved by taking several radiographs from different angles. However, this implies that the ability to locate a flaw is affected by the specimens size and shape.

X-radiography is not as shape limited as ultrasonic techniques. Sensitivity of the radiograph is proportional to ~1% of the specimen thickness, therefore a more accurate flaw detection is attained with thinner material. It is also possible to detect defects which are parallel to the surface with this technique.

The principal advantages of x-rays are the ability to examine complex shapes without contact. The technique can be used on both porous and dense material and detection can be done at any and all stages of processing. The limits of the technique are inadequate image contrast, the x-rays can not detect small cracks, low density inclusions, and defect/matrix couples of similar atomic number. The defect type can not be determined, and it is difficult to locate the position of the defect in space. Further developments include enhancement of surface crack resolution through the use of dye penetrant, and new techniques for three-dimensional detection. X-radiography even with its limitations is a relatively practical method for flaw detection.

Neutron Radiography. Neutron radiography operates in much the same way as x-radiography. The sample is radiated with neutrons and the image is recorded on film.[2] Flaws are detected by variations in the intensity of the transmitted beam on the film. The best source for neutrons are nuclear reactors, therefore this is not a technique that can be used on the production line. However, neutrons can magnify the contrast between elements. Defects which can not be seen with x-rays are discernable with neutrons. Therefore, neutron radiography is an excellent research tool.

Dye Penetrant. Dye penetrant aids in the visual detection of surface flaws. Dyes are absorbed into surface cracks making them more visible and therefore detectable.[3] The process involves a

cleaning step to remove surface oils and other contamination. Next, the surface is coated with dye and the dye is allowed to soak in. the remaining dye is removed leaving only the dye absorbed in the surface defects. The visibility of the remaining dye is enhanced by a developer which draws residual dye to the crack surface or via ultraviolet fluorescence.

Dye penetrant methods provide a simple low cost, effective method for examining surface flaws. It can be used on specimens of almost any geometry. The major drawback lies in the fact that it is only a surface technique and therefore does not provide a means of examining bulk flaws.

Optical Methods

Holography. Holographic NDE can detect extremely small on the order of a wavelength of light near surface defects as the result of an external stimulus. Abnormalities in the surface and near surface region can be detected by comparing a "perfect" holographic defect-free image with a part of known defect concentration to determine the sensitivity of the technique.

A number of methods are used to induce a holographic image. Vibrational shakers and piezoelectric transducers are used to generate a standing wave pattern, the frequency can be varied to resonate with the structure or defect. Careful selection of the frequency and anchoring is essential for NDE. Thermal and mechanical methods are also used to generate an image. Holographic techniques are extremely dependent on the design of the component

and the way in which the external stimulus is applied.

Holographic NDE is another method for determining small surface and near surface flaws. The technique allows rapid inspection of large areas. However, holography is extremely geometry specific and new techniques must be designed for each structure/defect type. This method can be adapted to a production environment if the part is vibrationally isolated. Lasers have been used in a production environment to generate interferometric fringe patterns for holographic NDE.

Visual. Visual NDE is probably the oldest and most commonly used inspection method. Although it is limited to approximately 20x size defects it is by far the cheapest and simplest method for determining large surface flaws.

Thermographic Methods

Infrared Thermography. In thermographic NDE an external force is applied to generate a thermal gradient within the part. The mechanical, thermal, or acoustic stimulus induces the thermal gradient which is used to determine defects in the surface and subsurface of the part. Equipment is used to resolve temperature distributions in the test specimen. Gradients of 0.1°C and spatial resolution of 0.1mm have been obtained on composite materials.

Defects are detectable at the surface or subsurface if they can produce frictional heat. Reproducibility and sensitivity of the test results are specific to the part configuration, defect type,

and to the vibrational energy applied. These techniques are best suited to materials with low thermal conductivity.

Photoacoustic Spectroscopy (PAS)

PAS converts a chopped, focused light beam into heat when it strikes an absorbing surface. The surface then expands (thermal expansion) and the mechanical impulse is converted to sound at the chopping frequency. The sound is then amplified and either a microphone or a transducer is used to detect the signal. Defects are located via phase detection, thus the portion of the signal coming from a given location in the specimen is determined.

This technique is sensitive to flaws, inclusions, defects, and impurities which cause variations in the materials thermal properties. Flaws on the order of micron sizes can be determined in this method. Some successful testing of ceramic turbine blades has been done with this technique, however, further development is necessary to bring this technique to an industrial level.

Proof Testing

Proof testing, although not entirely non-destructive, is a method of eliminating weak components before service. Ceramic components are stressed to levels above those expected in service to break the weak or flawed components. Proof testing is carried out in an inert environment and unloading rates are rapid, this reduces the chance of cracks formed during the test growing to critical size.

When a closely controlled environment and rapid unloading are used, proof testing is an effective method of evaluation. The difficulties lie in the possibility of inducing critical flaws through the test, and as yet not fully developed theoretical basis for predicting component behavior in service.

Summary

Many more NDE techniques exist, scanning laser acoustic microscopy (SLAM), scanning photoacoustic microscopy (SPAM), electrical and magnetic techniques and many variations on all these methods. All these techniques have limitations. Table 10.1 provides a summary of the applicability of some of these methods to ceramic materials. Many are only applicable to the surface of the component, are limited by part geometry, or can not be used to determine the characteristics (size, location, or type) of defect present. The minimum flaw size for several of these methods is listed in Table 10.2.

As yet, there is no "good" method for detecting all types of flaws in ceramics. Many of the methods are not applicable to the production line or are simply too costly and time consuming. Development of new and better technique will be required to accurately predict the reliability of ceramic components.

Table 10.1. Comparison of Several NDE Techniques for Flaw Detection in Silicon Carbide Heat-Exchanger Tubing.[4]

Method	Relative Effectiveness for Flaw Detection: Surface Cracks ID	Surface Cracks OD	Surface Pitting ID	Surface Pitting OD	Subsurface Inclusions	Subsurface Voids	Effectiveness for Characterization of Detected Flaws	Adaptability to Tube Geometry	Adaptability to Preservice Examination	Adaptability to In-service Examination	Reliability of Technique	Extent of Development Required for Commercialization	Relative Rate at Which Tubes Could Be Inspected
Acoustic Microscopy	G[a]	E	G	E	G/E	E	E	F	G	P	G/E	high	slow
Dye-enhanced Radiography	G	G	G	G	·	·	G	G	E	P	G	some	slow
Conventional Radiography	F	F	G	G	G	G	G	G	E	P	G	none	slow
Conventional Ultrasonic Testing	G	G	G	G	G	G	F	F/G	E	G	G	some	fast
Overload Proof Testing	G	G	?	?	?	?	P	P	P	·	F	some	fast
Holographic Interferometry	?	G/E	P/F	P/P	·	·	E	F/G	G	P	E	very high	fast
Infrared Scanning	P	P	P	P	P	P	P	E	E	G	G	some	fast
	effective measure of heat transport properties												
Internal-friction Measurement	F	F	?	?	?	?	P	P	P	P	P	very high	slow
Fluorescent Dye Penetrant Testing	·	G	·	G	·	·	F	E	E	P	G/F	none	slow

[a] For tubes with wall thickness ≤3 mm.
E = excellent; G = good; F = fair; P = poor; · = not applicable.

Table 10.2. Estimated Sensitivity of NDE Methods for Flaw Detection in Silicon Carbide Heat-Exchanger Tubing.[4]

Technique	Smallest Anomalies Detectable
Acoustic Microscopy	Flaws $\leq$ 100 μm long
Holographic Interferometry	Flaws $\leq$ 100 μm long (with lens techniques)
Dye-enhanced Radiography	Surface flaws with depth = 0.5 % t
Infrared Scanning	2% variation in thermal conductivity
Conventional UT	Surface flaws $\sim$ 100 μm deep

References

1. "Reliability of Ceramics for Heat Engine Applications," National Materials Advisory Board, NMAB-357, Washington, D.C., 1980.

2. Broz, A., and Brockelman, R., Private Communication, Army Materials and Mechanics Research Center, Watertown, MA, Nov. 1983.

3. "Nondestructive Evaluation of Metal Matrix Composites," National Materials Advisory Board, NMAB-413, Washington, D.C., 1983.

4. Kupperman, D.S., Deeninger, W.D., Lapinski, N.P., Sciammerella, C., and Yuhas, D., "Nondestructive Evaluation Techniques for Silicon Carbide Heat-Exchanger Tubing," Proceedings of DARPA/AFML Review of Progress in Quantitative NDE, AFWAL-TR-8-4078, July 1980, pg. 700.

11. INSTITUTIONAL BARRIERS TO EXPANDED ADVANCED CERAMICS USAGE

Advanced ceramic materials must overcome substantial institutional barriers, if they are to realize their true market potential. Many of these technical and institutional barriers have been discussed in the various applications sections of this report. Some of the major generic problems confronting expanded advanced ceramics usage include an inadequate data base, a lack of appreciation and confidence on the part of mechanical and design engineers, and a lack of domestic end-user support for structural applications. Development of a data base, improved testing techniques, education in ceramics manufacture and use, as well as codes and certification are required to expand future usage of advanced ceramics in the full range of applications.

Data Base Requirements

Probably the largest single constraint to expanded structural usage of ceramics is the poor quality and limited availability of information on the properties of these materials for purposes of engineering design and use. In a recent article on the "Mechanical Properties of Ceramics for Design Purposes," the following points were made:[1,2]

(1) Ceramics tend to have fairly specialized advantages for particular applications, but disadvantages tend to be generalized or ignored.

(2) The available data on commercially available materials are generally of poor quality, and methods of measurement are not standardized.

(3) Designers do not usually have a knowledge of the properties of ceramics and how to design with them. Improvements in awareness and understanding could lead to greater advantage being made of this class of material which are readily available at low unit cost.

The poor quality of available data is due to the fact that mechanical, thermal, and chemical properties of ceramic materials vary with the method of manufacture, Table 11.1 and 11.2. In addition, the measured values of these properties vary with the specific test method used. However, DOE is funding ongoing work at the Illinois Institute of Technology Research Institute to characterize a wide range of SiC and Si_3N_4 materials made by a number of manufacturers. This work uses a wide range of testing techniques on commercially available products which provides an excellent beginning to forming a larger data base for ceramics materials as a whole.

Mechanical failure in ceramics is due to the presence of defects. These defects are introduced throughout the entire process from powder processing, forming, and sintering, through product finishing operations. Tables 11.3 and 11.4 illustrate the influence of the surface finish and forming route on the strength of alumina.[3] It is the lack of control of the size, shape, and distribution of defects which generates the wide distribution of measured fracture

Table 11.1. Properties of Ceramics and Metals.[3]

Material / Property	Alumina	Carbon		Silicon Nitride			Sialon	Silicon Carbide		
		Low Density	High Density	Pressureless Sintered	Hot Pressed	Reaction Bonded	Reaction Sintered	Pressureless Sintered	Hot Pressed	Self Bonded
Bulk Density	3.98	1.61	2.50	3.08	3.18	2.75	3.00	3.10	3.21	3.10
Open Porosity (%)	0	37	0	0	0	5	0	0	0	0
Flexural Strength (MPa) RT 1,000C (4-Point)	440 340	13 13	70 70	650 470	845 680	298 300	355 355	500 475	930 820	530 530
Young's Modulus (GPa)	360	18	118	230	310	160	231	303	440	410
K_{IC} (MN/m$^{3/2}$)	4.5	–	–	5.3	5.8	3.6	2.2	2.4	4.4	4.6
Creep Resistance (MPa)	100 (1,000hr 1,200C)	–	–	280 (1,000hr 1,000C)	–	250 (1,000hr 1,000C)	–	350 (1,000hr 1,000C)	–	–
Linear Thermal Expansion Coefficient (x10^{-6}/C)	8.1	1.2	2.0	3.3	3.28	3.0	3.0	4.3	4.8	4.3
Thermal Conductivity (cal/cm · sec · C)	0.07	0.003	0.010	0.070	0.048	0.048	–	0.14	0.19	0.16
Heat Capacity (cal/g · C)	0.2	0.12	0.17	0.19	0.17	0.19	–	0.20	0.20	0.20
Thermal Shock Resistance Parameter R=Si/E · α	150	680	300	860	830	620	510	380	440	300
Oxidation Resistance (mg/cm^2)	–	–	–	0.1 (100hr 1,000C)	<0.1 (100hr 1,000C)	2 (100hr 1,000C)	–	<0.1 (100hr 1,000C)	1.5 (16hr 1,600C)	–
Melting Point (C)	2,030	1,440	1,450	1,900 (decomp.)	1,900 (decomp.)	1,900 (decomp.)	–	2,700 (decomp.)	2,700 (decomp.)	2,700 (decomp.)
Max. Use Temperature (C)	1,800	1,200	1,200	1,400	1,500	1,500	–	1,650	1,650	1,650

From: NGK Insulators

Table 11.2. Mechanical Property Comparison - Polycrystalline PSZ.[3]

Material	ρ (g/cm³)	H (GPa)	σ (MPa)	K_{IC} (MPa-m$^{1/2}$)	γ_f (J/m^2)	E (GPa)	ν	ΔT_c (°C)	Microstructure and XRD Phase Analysis
A. JAPAN (Y_2O_3)	5.75	11.7	900	4.7	50	201	0.32	375	0.1 - 0.5 μm 2-10μm duplex, cubic, tetrag. same monoclinic
B. AUSTRALIA (MgO)	5.75	9.4	700	>8-15	>160	200	0.24	425	10.40 m, 0.1-0.3 μm precipitates; cubic, tetrag., monoclinic
C. GERMANY (Y_2O_3)	5.77	11.6	650	>7 - 8 -15	>120 >500	209	0.31	325	similar to "D".
D. U.S.A. (Y_2O_3)	5.24	11.0	200	2.7 - 2.9	21.25	170	0.29	-	5-20 μm, no precipitates cubic ?
E. U.S.A. (M_9O)	5.08	10.3	300	6.0 - 6.1	111 - 115	162	0.27	350	1-10 μm, 0.1 μm precipitates monoclinic, cubic and tetragonal
F. U.S.A. (M_9O)	-	9.2 -11.5	430	4.7	60	192	0.30	225	55 μm, precipitates 0.1 - 0.3 μm

FROM: U.S. NAVAL RESEARCH LABORATORIES

Table 11.3. Strength as a Function of Surface Finish on Sintox FA 95% Alumina Die Pressed Tile Material.[2]

Surface Finish	No. of Samples	Mean Strength MNm^{-2}	Weibull Modulus
Diamond saw cut (as rec'd edges)	20	278	14.5
Diamond saw cut + anneal 1350/4h	20	215	5.3
Diamond saw cut, then diamond ground across length, 180 grit	19	194	7.4
do. + anneal 1350/h	19	190	9.3
do. + fine ground + lapped (7μm diamond)	23	280	10.7
do. + fine ground + lapped + anneal 1350/h	24	224	14.6
do. + rumbled 2h	10	224	8.6
do. + rumbled 10h	10	217	8.2
As received surface of rumbled tile (saw cut edges)	19	216	7.8

All specimens cut from die pressed tiles 50 x 50 x 5mm and tested with the pressing direction parallel to test face, except for last item in table in which the pressing direction was perpendicular to the test face. All tests on 40 x 5 x 2.5mm specimens, 4 pt bending at 25°C, strain rate 7.5×10^{-6} sec^{-1}.

Table 11.4. Strength as a Function of Forming Route on Sintox FA 95% Alumina Material.[2]

Forming Route	Test Specimen	Test Surface Finish	No. of Samples	Mean Strength MNm^{-1}	Weibull Modulus
Rod die pressed nominally 30 x 4 ϕ mm	As rec'd rod	As rec'd (tumbled)	26	236*	12.2
do.	Flats ground giving pseudo-rectangular section	180 grit across length	26	187*	8.5
Iso pressed, blank machined into discs before firing	Test bars cut from disc	180 grit ground across length of test bar	18	218	8.7
Slip cast plate cut into square tiles before firing	Cut from tile, test face perpendicular to tile face	180 grit ground across length of test bar	19	247	8.0
Extruded rod 4 ϕ mm	As rec'd rod	As rec'd	20	356**	6.7
do.	Flats ground giving pseudo-rectangular section	180 grit across length	15	324**	16.2
do.	do.	do. but ground parallel to length	19	357**	15.9

Test conditions as Table 1 but * tested on 20 mm span, strain rate 2×10^{-4} sec^{-1}. * and **, no correction for different effective test volumes or surface areas, compared to rectangular section bar tests.

stresses in otherwise identical test bars. Time under load, temperature, chemical environment, and stress state also affect the measured mean strength and its distribution.

Ceramic materials are generally more corrosion resistant than most metals. The chemical stability of ceramics is a function of many factors including composition, structure, grain size, and porosity. Table 11.5 illustrates the chemical resistance of various ceramics to a number of chemical reagents.[2] The corrosion performance of ceramic materials is also a function of time, temperature, and test environment.

The actual causes and mechanisms of ceramic failure are not well understood. What is critically needed is:

(1) a systematic data base, that is material and process specific;

(2) an expanded data base that is time, temperature, and chemical environment specific;

(3) standardized test procedures; and

(4) a fundamental understanding of the factors which affect properties and performance.

Designer Preference

Product design engineers select materials of construction on the basis of past experience and available data. Few structural design engineers have any experience with ceramics and reliable data is scarce. Formal codes and specifications for ceramics exist in traditional applications (refractories, abrasives and structural

Table 11.5. REsistance of Ceramics to Chemical Attack - Crucible Tests.[2]

Material	Supplier/Grade	Reagent	Steam	HCl 35%	H_2SO_4 98%	HF 40%	KOH 10%	$NaNO^*$	EP*	Y_2O_3*	AL**	Y_2**
		Temp °C	1200 700±5	Boiling		Boiling	23°C	60°C	500°C	900°C	400°C	400 °C	500°C
		Time	24h	30m / 2h	30m / 2h	24h	168h	24h	4h	24h	24h	12h
99.5% Alumina	Frost-Degussit 'AL23'	A	A(C)	A(C)	C	A	B	D	D	A	B
Magnesium Silicate	Vesgo	B	A	A	D	B	D	D	D	D	C
Vitreous Silica	Vitrosil /Thermal Syndicate Ltd.	B	A	A	B	C	D	D	C	D	C
Porcelain stoneware	Frost-Degussit Zamotec ER23'	A	B	C	D	A	C	C	D	B	C
Reaction Bonded Silicon Carbide	REFEL' Borax Morgan Foseco	B	A	A	A	C	D	D	D	D	C
Reaction Bonded Silicon Nitride	2.5 grade, A.M.E Ltd	A	A	A	C	A	D	D	D	A	C
Hot pressed Si3 on Nitride	A.M.E. Ltd.	B	A	A	C	A	D	D	D	A	A
Recrystallised silica	Press Corning	B	A	A	D	C	D				C

Key Extent of attack based on appearance and weight loss A = no attack detected (by methods used), B = slight attack, C = moderate attack, D = severe attack, * at one atmosphere, ** at fluidised argon atmosphere.

clay products), however only recently has SiC been specified as a seal material. Current codes for many potential advanced ceramics applications do not include ceramics as potential materials. Standards have focused on materials presently in use, in most cases metals.

Current and future engineers and designers must be advised as to the advantages and disadvantages of ceramic materials in structural applications. Currently, materials courses are not generally required for engineering students and when materials are part of the curriculum, the emphasis is on metals. Inter-disciplinary courses on designing with brittle materials are available to materials engineers, but are not generally required of design engineers. Courses at the college level, and mini courses for continuing education on design with brittle materials should be offered and publicized. An attempt to develop an awareness of materials capabilities in design as well as the ability to design for a specific application is needed.

The ceramics industry and professional institutions have the necessary expertise to provide the required data base. The responsibility for generating this science/knowledge/data base must be shared by the material supplier as well as the consumer, represented either directly or indirectly by federal proxy. There is definitely a role for the National Bureau of Standards to play in developing and standardizing testing techniques. Current Research at the Bureau is investigating new non-destructive evaluation techniques which show promise for ceramics, however further effort

will be required before reliable techniques are commercially available.

The recent public and professional media attention being given to advanced ceramics as the new super material is akin to the press given plastics in the 1960's. Public awareness will continue to expand as consumer products such as scissors and turbochargers are introduced to the marketplace. Unlike plastics, ceramics are not perceived as being cheap, but instead as having inherent value in chinaware and artwork. Ceramics are also perceived as brittle and fragile. An awareness that advanced ceramics are an engineering material that can be mass produced at a reasonable cost is needed by the public and the traditional ceramics industry.

In many ways the traditional ceramics industry has provided its own barriers to the future development of advanced ceramics. The traditional industries, refractories, abrasives, structural clay products and others have been stable and profitable. Recent trends in the U.S. economy have depressed the traditional industry (for example the refractories industry is closely tied to domestic steel production), and competition from abroad, mainly Japan, is forcing the industry to examine new possibilities and products. Most of the changes in industry appear to come from end-users rather than the producers themselves. Ford Motor Company's work on the automotive gas turbine led to the development of a new Si_3N_4 cutting tool. The Gas Research Institute is funding research at a number of ceramics and turbine companies to promote the development of high quality ceramic materials (SiC tubes) for industrial heat exchangers.

Ceramic heat exchangers should encourage the usage of natural gas. Until recently, many of the traditional ceramics companies ignored the potential for advanced materials. However, as the perceived demand grows, companies with a strong base in ceramics will begin to focus on advanced ceramics. This will be a slow process both in terms of industry awareness and current economic conditions.

Environment, Health and Safety

Substitution on a large scale of one material for another requires a careful assessment of the impact on the environment, health and safety in conjunction with purely technical considerations. Because the ceramics industry has a large traditional base, standards have been set by both the Environmental Protection Agency (EPA) and the Occupational Safety and Health Administration (OSHA). Both these agencies collect data and statistics related to environmental effects and health and safety respectively. Although the ceramics industries covered in these studies are not precisely the same as those that would be used as substitutes for critical materials, some generalizations can be inferred from these data.

EPA maintains a priority listing at the major stationary pollutant sources.[4] This list goes from the worst (1) to least (59) critical source. Metallic mineral processing and Steel and Gray Iron foundaries rank 14 and 17, respectively. Glass is 33rd on the list, Brick and related clay products are 46th and several other ceramic categories have been deleted from the list. The major

sources of pollutants are NO_x gases in glass manufacture[5], and SO_x and particulates from all ceramic processes.[6] Although SiC and Si_3N_4 production are not specifically cited, it is not unrealistic to assume that their level of pollution would be of the same order of magnitude as other portions of the ceramics industry. Therefore overall environmental effects from the use of ceramics should be less than those for equivalent levels of metal production.

It is more difficult to assess the effects of ceramics production on health and safety. From statistics provided by OSHA,[7] it appears that total lost work days for 1980, 1981, and 1982 in many portions of the ceramics industry are not significantly different than those in metal producing industries in the same years. However, injury and illness statistics do not specify particular causes or their relationship to a specific industry. There is some hazard associated with every manufacturing process, but it is not possible to determine from the present data if expanded use of ceramics would improve upon existing hazards associated with metal processing. However, it does not appear that ceramics would be worse.

Institutional Requirements

The lack of reliable data on the properties and performance of ceramic materials has been and continues to be a major constraint to expanded acceptance and use of these materials in the United States. This situation is directly attributable to the conspicuous absence of an industrial association or organization charged with research,

development, or product data specification. There is no ceramic equivalent to the Aluminum Association, American Iron and Steel Institute, or International Lead and Zinc Research Organization to focus research efforts, provide standardized data, and promote ceramic materials. The ceramics community is also divided into sub-critical groups by market sector. Few domestic companies have major resource commitments to advanced ceramics and those that do, such as IBM, hold technical advances in ceramics as a priority to the larger systems technology, such as advanced computer technology. In addition, there is no national laboratory or Bureau of Mines equivalent to promote and focus research and development efforts in ceramics. The 10-15 universities with programs in ceramics are also insufficient to meet the educational and research requirements of this rapidly expanding field. The American Ceramic Society does provide a forum for the exchange of technical information, but only recently has it begun to collect any data on industry production or a standardized data bank.

The Japanese ceramics industry, recognizing this void and need, established the Japanese Fine Ceramics Office through MITI in July 1982. The primary objectives of this Office are to provide a comprehensive picture of the Japanese advanced ceramic industry, systemize the industry, consolidate the industry's foundation, and adopt comprehensive policies designed to promote sound growth. Two of the major activities of this Office are the promotion of the establishment of standardized ceramics testing methods and a study of the requirements of an advanced ceramics test center which would

collect, generate, and distribute standardized property data.

The U. S. government, through its agencies, government laboratories, and the military has funded a number of programs for ceramics in the areas of heat engines, heat exchangers, and basic science. Other institutions, the Gas Research Institute, and major companies are expanding their level of advanced ceramics research. However, if ceramics are to become the "material of the future" there must be a greater concentration of effort. This effort should focus on developing ceramics for uses in both industrial and strategic materials substitution. Ceramics provide excellent wear resistance and thus could provide increased productivity in the machining industry, chemical process industries and metal process industries where wear and corrosion resistance are critical. Ceramics can greatly increase the energy efficiency of many industries which use high temperature processing. Finally, when the major technical barriers are overcome, ceramics could be used for their high temperature strength again resulting in significant fuel savings and increased productivity.

References

1. Creyke, W.E.C., "Mechanical Properties of Ceramics for Design Purposes," Materials in Engineering Applications, Vol. 1, no. 3, pp. 143-42, 1979.

2. Morrell, R., "Engineering Ceramics -- Property Data for the User," Materials in Engineering, Vol. 2, Sept., pp. 15-20, 1980.

3. Kamo, R., "High Technology Ceramics for Japanese Heat Engines," Report Draft, Division of Policy Analysis, Advanced Technologies and Resources Policy Group, National Science Foundation, April, 1983.

4. "Revision to the Priority List of Categories of Stationary Sources", Federal Register, Rules and Regulations, AD-FRL-1990-5, Environmental Protection Agency, Vol. 47, No. 5, Friday, Jan. 8, 1982, p. 950.

5. Reznik, Richard B., "Source Assessment: Flat Glass Manufacturing Plants", PB-252-356, Monsant Research Corporation, Dayton, Ohio, March 1976.

6. "Source Category Survey: Refractory Industry", United States Environmental Protection Agency, office of Air Quality Planning and Standarys, Research Triangle Park, NC, EPA-450/3-80-006, March 1980, pp. 3-5, 22.

7. Ilma Rosskopt, Occupational Health and Safety Administration, Personal Communication, Dec. 1983.

12. PROSPECTS FOR ADVANCED CERAMICS

Technical Factors

Cobalt and chromium are used primarily as alloying elements to impart high temperature strength, chemical stability, and wear resistance to steels and nickel-based superalloys. However, it is no match for ceramic materials which intrinsically possess superior high temperature strength, chemical stability, and wear resistance. As illustrated in Table 12.1, silicon nitride and silicon carbide maintain higher strengths than superalloys at temperatures above 1350°K.[1] Consequently, these materials can be considered seriously for structural applications at these temperatures. In addition, these ceramic materials have roughly a third the density of superalloys which provides an additional advantage when used in rotating or reciprocating applications. In other applications where strength is secondary and high temperature dimensional control is a priority, magnesium aluminum silicate (MAS) is of interest with its very low thermal expansion coefficient. In addition, zirconia and aluminum titanate make excellent thermal barriers with their low thermal conductivities. Unfortunately, the brittle nature of these ceramic materials has severely limited their use as substitutes in high performance, stressed, structural applications.

With no inherent ductility, ceramic materials fracture without warning and usually result in the catastrophic failure of the device or component. Of critical importance is the fact that ceramic materials do fracture unpredictably at well below their real strength. Consequently, engineers are forced to design with

Table 12.1. Physical Properties of Ceramic Materials.[1]

Properties / Material	Bending Strength (at 800 K)	Bending Strength (at 1400 K)	Density	E-Modul (at 1260 K)	Thermal Expansion (300..1260K)	Thermal Conductivity (at 1260 K)
	MN/m^2	MN/m^2	$10^3\ kg/m^3$	$10^9\ N/m^2$	$10^{-6}\ m/mK$	W/mK
S-Si_3N_4	530	300	3,1	300	3,2	12
RB-Si_3N_4	300	300	2,6	180	3,0	9
S-Si C	450	450	3,15	400	4,5	40
MAS	70	20	2,2	12	0,6	1
$Zr\ O_2$	600	300	5,7	200	9,8	2,5
Al_2O_3-$Ti\ O_2$	40	20	3,2	23	3,0	2
inco 713 C	900	200	7,9	170	15,0	25

ceramics at a fraction of their real strength or eliminate them altogether in critical applications. This unpredictable failure mode is due to the presence of irregular micro- and macrostructural flaws and imperfections. These flaws are due explicitly to a lack of process control which results in irregular chemical and phase composition, as well as nonuniform grain size. In short, current ceramic powder processing and component manufacturing technologies are inadequate to provide the consistent microstructural control necessary to reliably produce high value-added structural ceramics.

This structural control problem can be better appreciated when you consider that a simple ceramic component is formed by a powder process that begins with more than 10^{12} particles per cubic centimeter. In current practice, these starting powders are typically impure, agglomerated, and have a wide particle size distribution, Figure 12.1. Traditional ceramic processing efforts have centered on sintering and grain growth control within these heterogeneously packed green microstructures in an attempt to control grain coarsening and void formation. Unfortunately, the mechanical forces applied to ceramic powders in greenware forming operations are smaller than the repulsive interparticle forces when dealing with submicron powders, Figure 12.2. Consequently, rather large voids are left in the greenware giving it an uneven density distribution. It is this lack of control of structural flaws and other impurities which generate warpage during sintering, lack of dimensional control, and microcracks in finished parts, thereby rendering advanced ceramic components unreliable and non-reproducible, Figure 12.3.

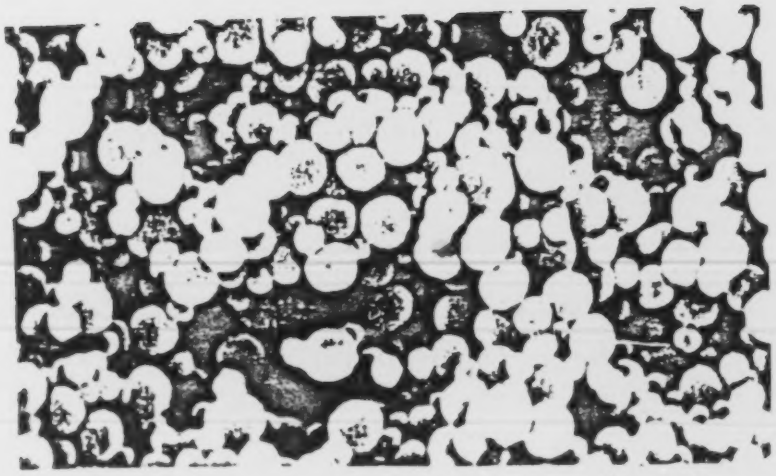


Figure 12.1. Typical ceramic green microstructure.

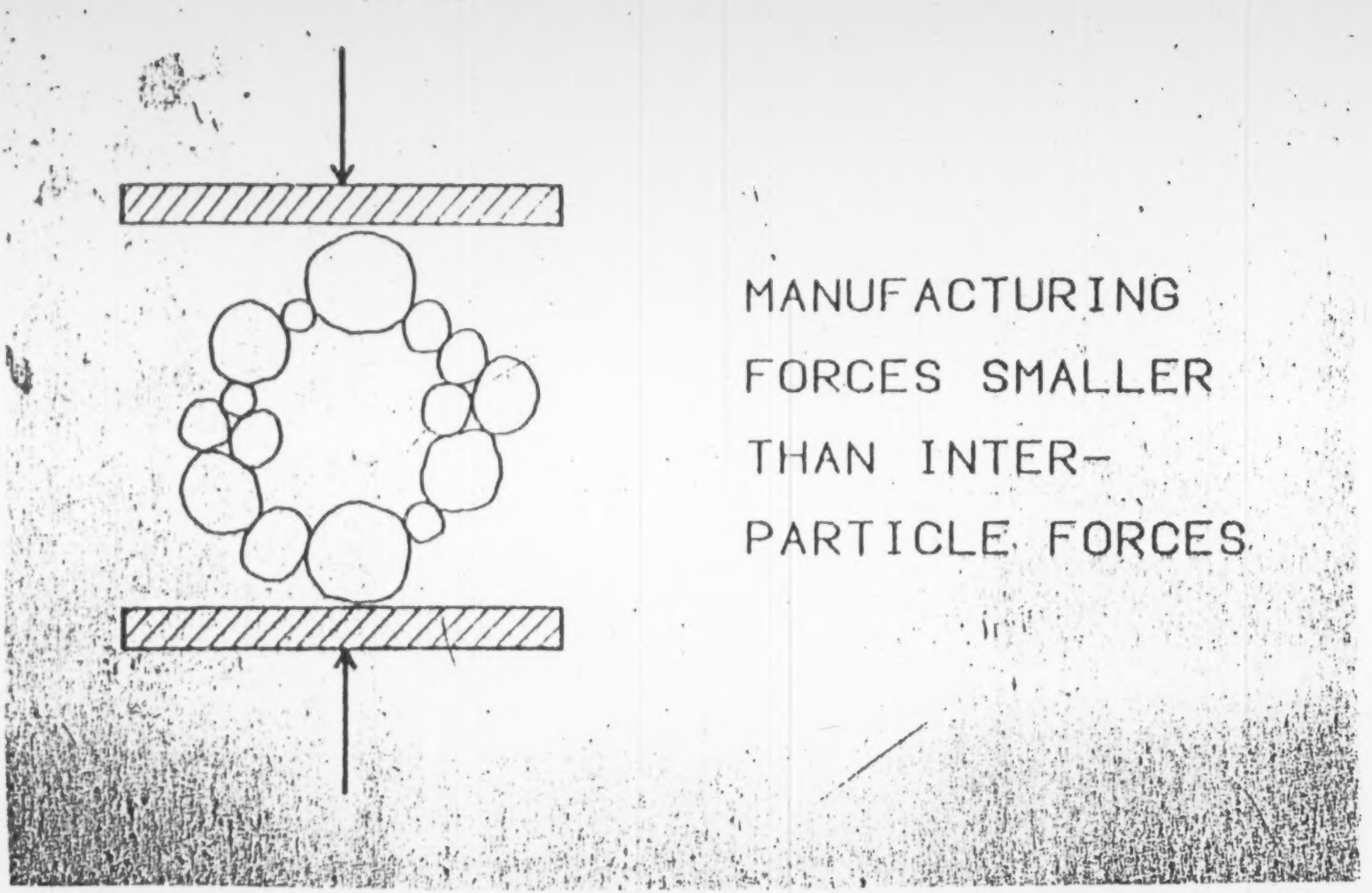


Figure 12.2. Manufacturing forces smaller than inter-particle forces.

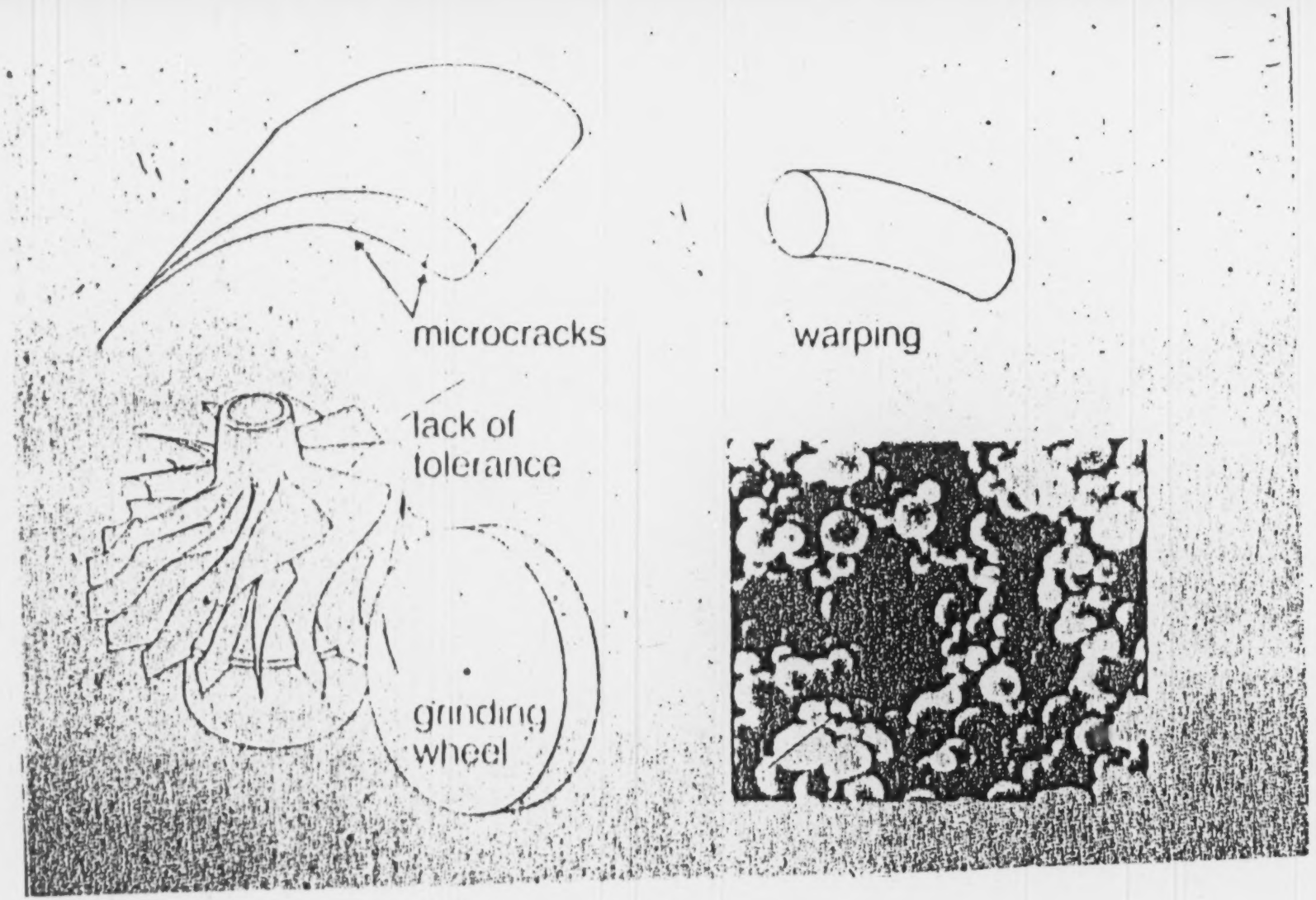


Figure 12.3. Effect of greenware structural flaws.

It is obvious that in order to produce reliable ceramic components, one must begin with the highest quality starting powders, form these powders into uniform high density greenware, and control the subsequent sintering process to ensure complete densification while maintaining control of the microstructure of the final part. In summary, the ideal ceramic powder process requires:

1. pure, unagglomerated, monosized, submicron powder starting materials;
2. uniform, close-packed green microstructures, and
3. proper selection and control of the thermochemical processing variables, such as pressure, temperature, and composition.

Such ideal starting powders, Figure 12.4, are currently being produced in experimental quantities by such processes as organochemical precipitation and laser induced gas phase synthesis.[2-5] When cast into dense, homogeneous green structures, these monosized, unagglomerated powders can be sintered to nearly theoretical density with uniform shrinkage to a near net final shape, Figure 12.5. In addition, the sintering process can be accomplished in considerably less time and at lower temperatures (1300°C versus the traditional 1700°C) than with traditional ceramics. With these ideal starting materials and the process control they facilitate, advanced ceramic components with enhanced properties could be reliably and reproducibly manufactured. Hence, the future potential of advanced ceramics hinges on the continued development and scale-up of ceramic powder production processes and

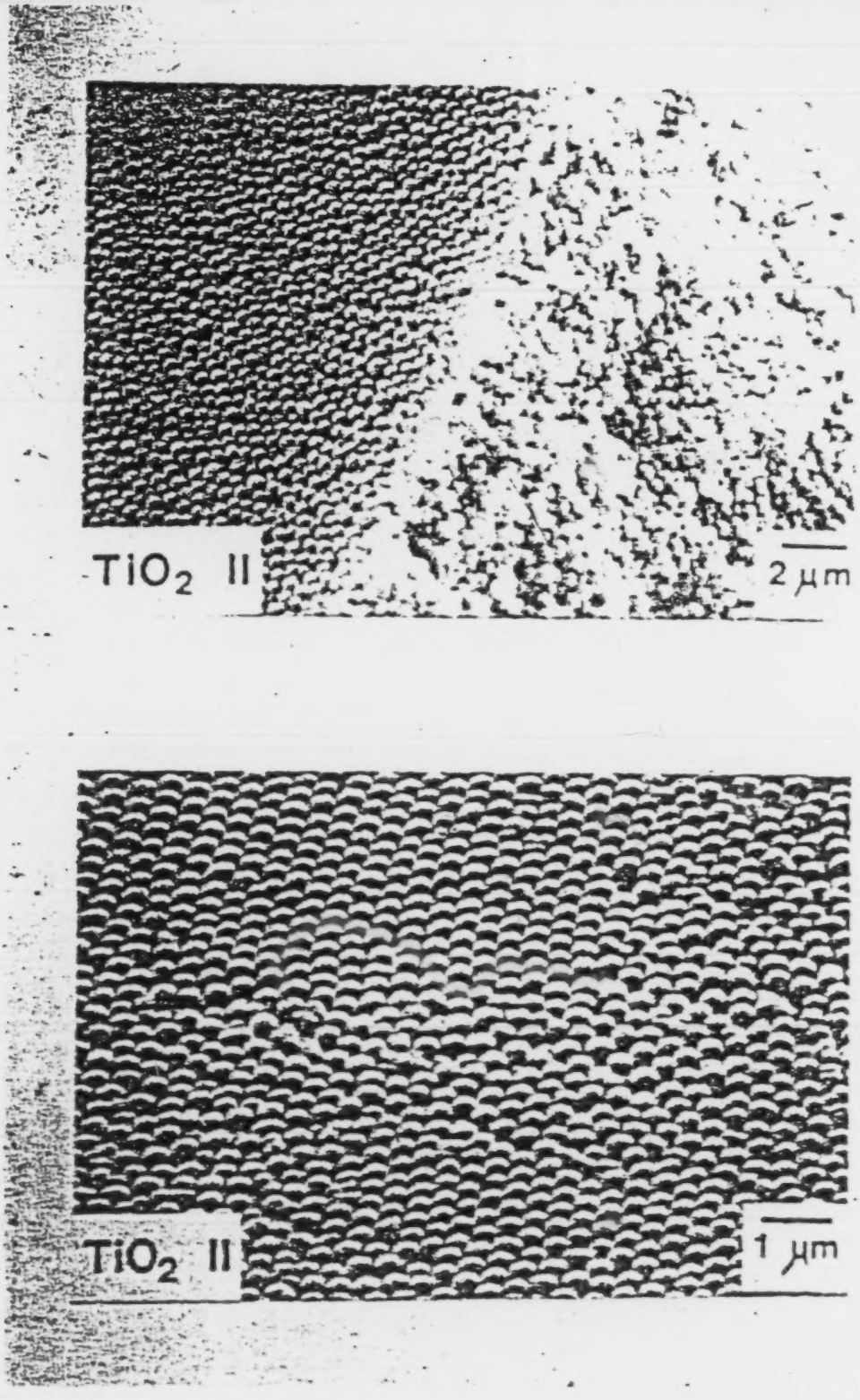


Figure 12.4. Submicron, monosized ceramic powders.

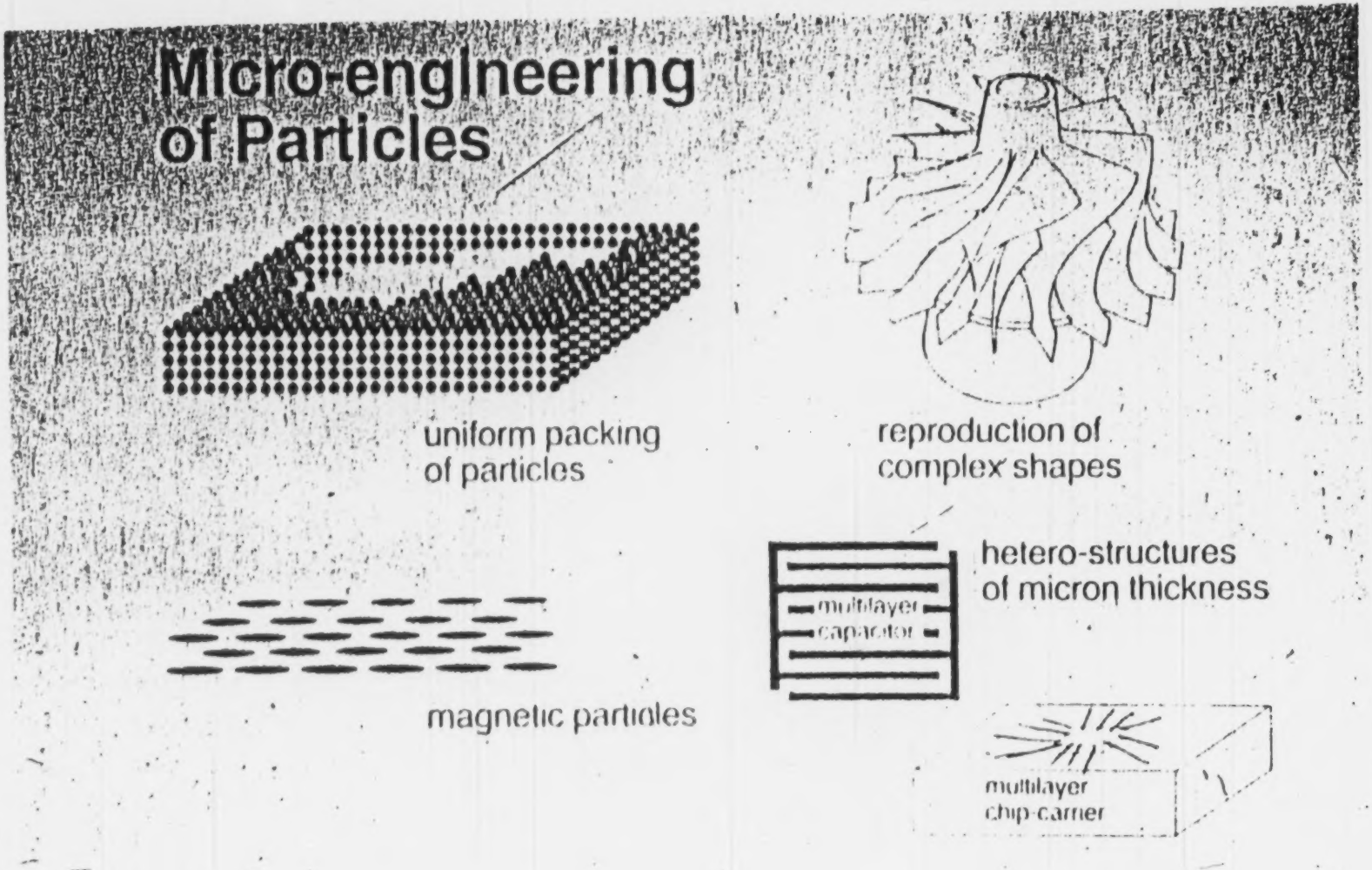


Figure 12.5. Fabrication with ideal, close-packed powders.

microstructural control of subsequent forming and sintering operations.

These advanced, high performance ceramics are, in fact, excellent potential candidates to replace strategic materials, in particular, those used in steels and superalloys for high temperature, wear and chemical resistance, structural applications. In one potential application in particular, small diameter automotive gas turbines, current superalloys have inadequate high temperature performance characteristics. Only high tech ceramic components appear to have sufficient high temperature performance characteristics to qualify as potentially viable materials of construction for both stationary and moving parts in this particular application. In substituting for superalloys, ceramics would reduce the demand for nickel and tungsten as well as manganese, chromium, and cobalt. In chemical ware parts and catalytic applications, advanced ceramics are also a potential substitute for platinum.

Some of the functions and uses of advanced ceramics are outlined in Figure 12.6 by function, property, and use.[6] Clearly, the potential economic and technological impact of advanced ceramics has far-reaching implications. With respect to the direct substitutability of high tech ceramic materials for structural metals, Japanese scientists believe that these materials have the potential to transcend metals in structural applications, Figure 12.7. Future high tech ceramic materials are expected to outperform superalloys with respect to heat resistance, high temperature

Figure 12.6. Function and use of fine ceramics (examples).[6]

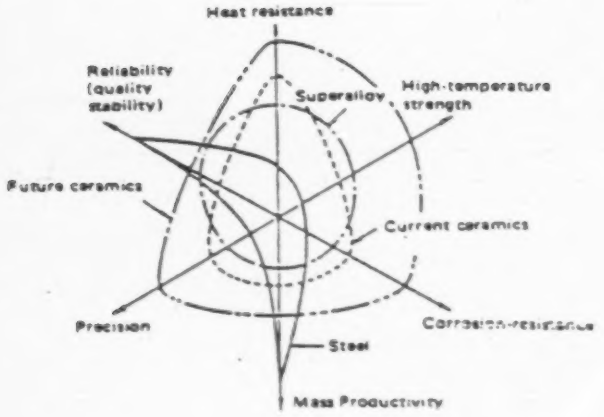


Figure 12.7. Performance parameters of ceramics as mechanical materials (Hiroaki Yanagida: Diversified Functions of Ceramics, Kagaku to Jikken (Science and Experiments), Nov., 1980, p. 13).

strength, corrosion resistance, mass productivity, precision, and reliability.

Economics of Advanced Ceramics

High technology or advanced ceramics are high value added materials which deliver superior mechanical, electrical, magnetic, and optical properties and performance. Many of these materials are based on readily available raw materials such as the oxides, nitrides, or carbides of silicon, aluminum, zirconium, and iron. The essence of the high tech ceramic business is that common starting materials are converted into high value added commodities and components by sophisticated high technology processing and manufacturing systems. The current worldwide market for advanced ceramics is estimated to be on the order of $4.25B, Table 12.2. Roughly half of this demand is currently being met by Japanese companies whose sales of advanced ceramics exceeded $2B in 1980.[7]

Electronics applications account for approximately 80% and 65% of the total market value of Japanese and world production of advanced ceramics, respectively. While this market offers significant growth potential, it is dwarfed by the potential size and impact of advanced ceramics in heat-resistant applications which include engine and turbine components. At present there exists no established technology for the mass production, testing, and application of advanced ceramics in high temperature engines. However, as part of the concerted Japanese research and development effort, Kyoto Ceramic and NGK Sparkplug are independently testing

Table 12.2. High Techonology Ceramics Markets (1980 - $M)*.[8]

Product	Japan+	World
Ceramic Powders	130	250
Electronic IC Packages/Substrates	540	880
Capacitors	325	750
Piezoelectrics	295	325
Thermistor/Varistors	125	200
Ferrites	380	480
Gas/Humidity Sensors	5	45
Translucent Ceramics	20	45
Cutting Tools: carbide, cermet, coated	120	1,000
non-carbide≠	5	25
Structural Ceramics (heat and wear resistant)	120	250
TOTALS	$2,065M	$4,250M

≠ For example, alumina, partially stabilized zirconia, silicon carbide and nitride, and oxynides.

* Excludes fibers, nuclear fuels, spark plugs.

critical engine components. A major component of the national materials research program in Japan is focussed on primary and secondary processing technology for ceramics.

The focus of advanced ceramics market growth to date has been on the electronics industry sector simply because this sector can absorb the high cost of these materials on a functional basis. For example, a ceramic IC substrate or package may cost roughly a dollar or so. On a per pound basis, this same component could cost several hundred dollars per pound. Clearly, such a cost would be prohibitive for a structural component such as an engine piston, cylinder liner, etc.

Table 12.3 examines the typical manufacturing cost structure for high value-added ceramic components. Roughly half of the cost of a typical ceramic component is due to rejects. This means that on average one ceramic component is discarded due to defects for each one that is sold. This fact puts the economic potential of advanced ceramics processing technology into perspective.

If uniform ceramic green structures could be formed from ideal starting powders, these structures could be sintered to end near final shape. Ceramic components sintered to near net final shape would require minimal finishing or grinding thereby reducing this cost factor. As mentioned earlier, uniform, close packed, high density green structures can be sintered to full density at lower than normal sintering temperatures in less than normal sintering time. This feature has significant potential to reduce the firing cost factor. Part shaping with ideal starting powders may be

Table 12.3. Typical Manufacturing Costs for High Value Added Ceramics

1.	Raw Materials (powders, chemicals, etc.)	15%
2.	Part Shaping (mixing, milling, casting, etc.)	15%
3.	Firing (binder burnout, sintering, etc.)	15%
4.	Finishing (simple grinding, joining, etc.)	5%
5.	Rejection at any step (1 through 4)	50%*

* The cost of rejection varies from product to product, but is generally in the range of 25-75% of the manufacturing cost.

possible with some modification to existing slip casting, injection molding, and other forming operations at little or no cost penalty. The raw material or powder production cost for new processes is more difficult to calculate. However, a preliminary cost estimate has been made for the laser induced gas phase synthesis process versus the Acheson process for making submicron silicon carbide powder, Figure 12.8. The cost of Acheson process silicon carbide increases rapidly with decreasing powder size due to the increasing comminution energy cost. The powder production cost of the laser process is independent of particle size because controlling the ceramic particle nucleation and growth process has no obvious consequence to equipment costs or mass flow rates.[4]

Assuming that laser processing and other techniques for producing ideal ceramic powders can be economically scaled to commercial production, the overall cost structure for these powders appears to be very promising. However, the largest cost savings potential rests with the ceramic component rejection rate. As discussed earlier, these ideal ceramic powders are expected to minimize microstructural defects and thereby increase component performance, reliability, and reproducibility. Consequently, the 50% reject cost factor identified in Table 12.3 could be drastically reduced or eliminated. The potential impact on substitution for critical materials as well as other commodities could be significant. If successful, high tech ceramic usage in automotive engines alone could research $30 billion on a worldwide basis at maturity which is anticipated for the year 2000 and beyond.[8]

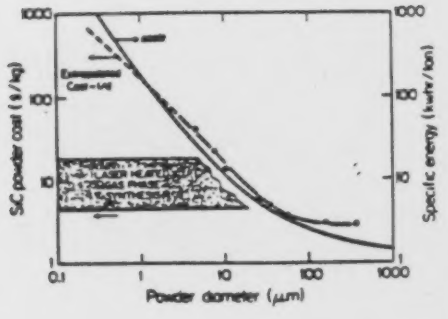


Figure 12.8. A comparison of SiC production costs.[4]

Global Efforts in Advanced ceramics

The present status and future requirements of advanced ceramics is best understood when viewed first from an historical perspective. A general comparison of the level of effort by various countries is presented in Figure 12.9.[9] The original research on silicon carbide and silicon nitride, two of the major contenders for structural applications, was conducted in the United States. However, Great Britain reported the first efforts to apply these materials during the 1960's. The first major U.S. effort to apply advanced ceramics was the Ford-Westinghouse study initiated by DARPA in 1971. Although the principal thrust of this project was to improve methodologies for designing with brittle materials, the ceramic gas turbine engine was used as a model. The early success of this program and the developing fuel crises led to additional support, as shown in Figure 12.10. This involved the expenditure of approximately $115 million, not including corporate funding, during the fiscal year period 1974-1981 and resulted in significant progress. At the Department of Energy Automotive Technology Development Contractors Coordinating Meeting in October 1982, contractors for AGT 100, AGT 101 and CATE presented conclusive results as to the feasibility of using ceramic components in automotive or truck engines. West Germany entered the picture in 1974. The West German effort has received extensive federal support and has focused on the development of automotive gas turbines and turbochargers. Major automakers such as Volkswagen are heavily involved.[1]

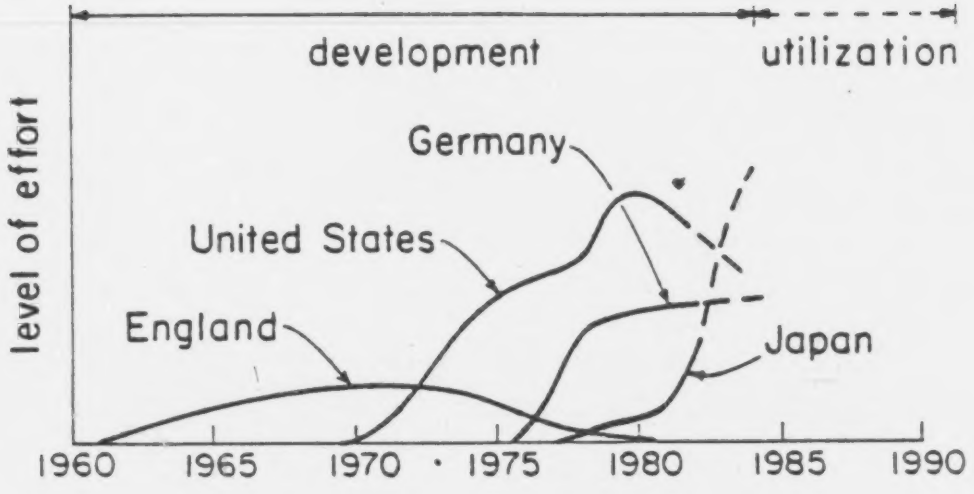


Figure 12.9. A generalized comparison of structural ceramics activity.[9]

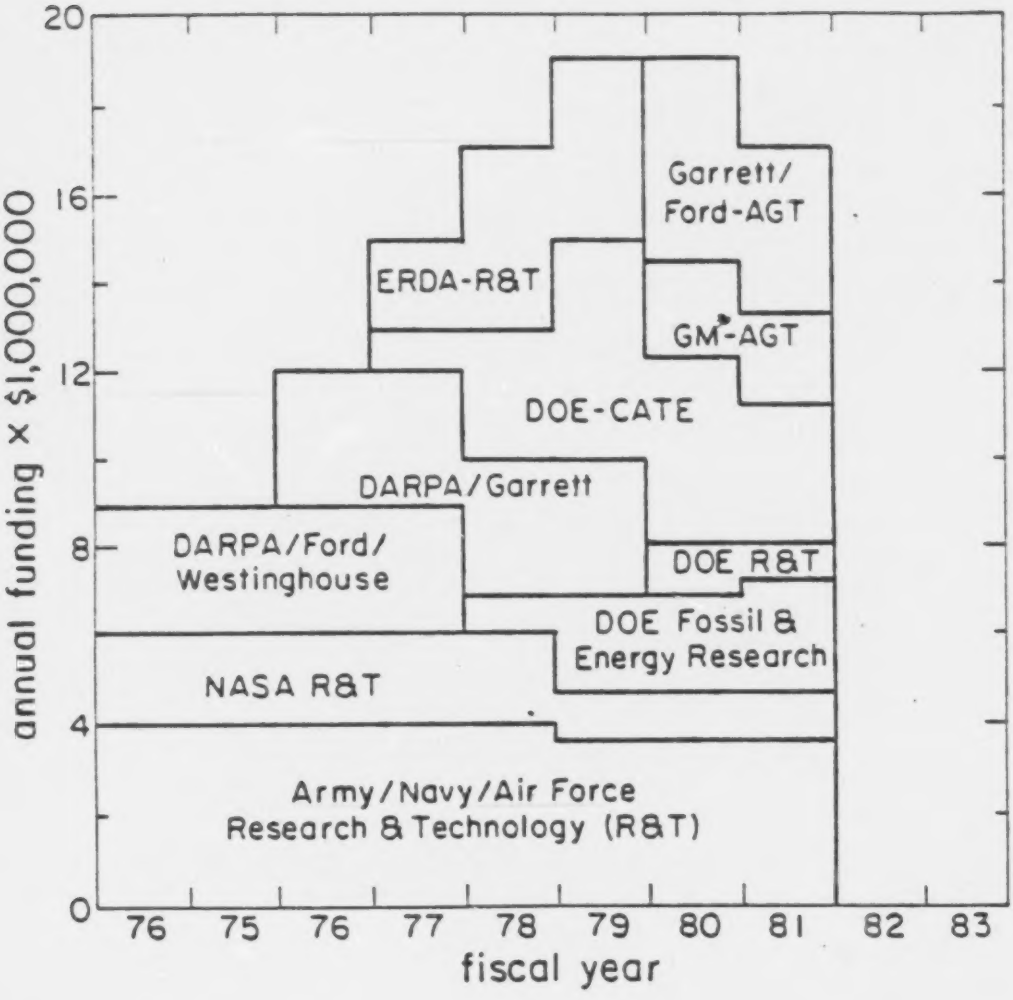


Figure 12.10. U.S. funding of ceramic gas turbine engine development, yrs. 1974-1981.[13]

The Japanese government and industry were rather late-comers in 1977. However, their collaborative effort is widely regarded as the best organized and financed in the world. The current advanced ceramics research and development effort of Japanese government affiliated laboratories and institutes is detailed in Table 12.4.[6] The private and collaborate government efforts of Japanese industry is much more extensive, but very difficult to quantify. The Japanese efforts are encouraged by their marketing success, Table 12.2, which includes a 20 percent expansion of output during the worldwide recessionary period between 1981 and 1983.[6]

The major difference between the advanced ceramics efforts of the U.S. and both Japan and West Germany is that the U.S. effort has focused on design methodologies while the others are focusing on materials supply and processing.[10] While the U.S. program has recently concluded that "Yes, ceramics do work in engines,[11] the West Germans and Japanese have been busy improving the quality of the basic materials and their processes which is reflected in current component performance and cost. Some observers now feel that because of the past U.S. emphasis on technical viability, with little attention being given to reliability and economic viability, that the U.S. no longer has a dominant worldwide position in this materials sector. This does not imply that the U.S. has lost its leadership with respect to the basic research and level of understanding of this technology, but rather that the U.S. is lagging in the development and exploitation of this important technology.

Table 12.4. R&D of Fine Ceramics by Government-Affiliated Laboratories and Institutes.[6]

Project System	R&D Project	Period (FY)	Participants
Science and Technology Agency			
Special R&D	Study on the development of ceramics dispersion and strenghtened fine materials	1981-1985	National Research Institute for Metals
	R&D of ultra high-temperature heat resistant ceramics	1980-1984 (1st phase)	National Institute for Research in Inorganic Materials
Ministry of International Trade and Industry			
Research and Development Project of Basic Technology for Future Industries	Fine ceramics (High performance ceramics)	1981-1990	Government Industrial Research Institute, Nagoya (GIRI, Nagoya) Government Industrial Research Institute, Osaka (GIRI, Osaka) Mechanical Engineering Laboratory National Institute for Research in Inorganic Materials Engineering Research Association for High Performance Ceramics
R&D on Energy Conservation Technology (The Moonlight Project)	Advanced gas turbine	1978-1984	Government Industrial Research Institute, Kyushu GIRI, Osaka GIRI, Nagoya Engineering, Research Associations for Advanced Gas Turbine
	Advanced battery energy and storage system	1980-1990	Electrotechnical Laboratory GIRI, Osaka New Energy Development Organization (NEDO)
	Magnetohydro-dynamics (MHD) generation technology	1976-1982 (2nd phase) 1966-1975 (1st phase)	Electrotechnical Laboratory GIRI, Nagoya GIRI, Osaka
Leading and Basic R&D on Energy Conservation Technology	Studies on energy conservation technology relating to infrared radiation and ceramic materials	1979-1982	GIRI, Nagoya
Special R&D	Research on application of the structure of ceramics	1980-1984	Mechanical Engineering Laboratory

Table 12.4. R&D of Fine Ceramics by Government-Affiliated Laboratories and Institutes.[6] (cont'd)

Project System	R&D Project	Period (FY)	Participants
	Research on generation and application of super high energy by high explosives (Explosive treatment of ceramic powder)	1980-1984	National Chemical Laboratory for Industry
	Research relating to super refractories and thermal-insulating ceramics	1976-1982	GIRI, Nagoya
	Study on development of high-performance high-melting inorganic material	1980-1984	GIRI, Nagoya
	Research concerning laser-related glass materials	1980-1983	GIRI, Osaka
	Research on production technology for new functional porous glass film	1981-1984	GIRI, Osaka
	Research relating to developing technology for high strength reflecting devices for ultraviolet rays	1982-1984	GIRI, Osaka
	Research on new material for cutting tools	1979-1982	GIRI, Osaka
	Study on development of carbon-ceramic composite material	1981-1984	GIRI, Kyushu
Ministry of Education			
Grant-in-Aid for Special Research	New investigation into functional ceramics	1982-1984	Osaka University, Kyushu University, etc.
Ministry of Transport			
Special R&D	Research on advanced gas turbine for ships	1979-1983	Ship Research Institute

The national effort on the part of the government, academic institutions, and industries of Japan to collaboratively develop and promote high technology ceramics represents a bold initiative to achieve technological and market leadership within the class of engineering materials. Advanced ceramics are expected to significantly influence the future of electronics, machining operations, automotive and utility powerplants, and processing and manufacturing system automation. Clearly, leadership in advanced ceramics technology and production will provide an enhanced competitive position in the international marketplace of the future.

The current challenge for ceramic industry leadership comes from Japan where ceramics are considered to be "a new generation of materials to replace metals". In 1981, MITI launched a 10-year program for the development of basic technologies for the next generation industry within which ceramics is one of the core programs. Given the recent national initiative in advanced ceramics research and development reflected in the formation of the Japan Fine Ceramics Association and the funding commitment of the Ministry of International Trade and Industry (MITI) of Japan, it is reasonable to expect Japanese advances in fine ceramic technology and production to accelerate significantly. Japan is firmly and uniquely committed to the long term development of advanced ceramics.

A principle motivation for the new national commitment to advanced ceramics in Japan was provided by the 1973 and 1979 oil crises. With no significant domestic energy supplies, Japan is currently dependent upon petroleum imports for more than 70% of its

primary energy needs. Prior to the oil shock, Japan's industrial structure and development policies emphasized energy intensive basic materials such as steel. These industries helped promote the rapid growth period of the 1960's. Faced with the current slowdown in worldwide economic activity and high energy costs, Japan is readjusting its long term industrial policy towards "softwarization" or a combination of knowledge-intensive secondary processing and service oriented industries. High value-added primary and secondary processing of high technology ceramics for electronic and heat and wear resistance applications in machine tool and engines meets these policy specifications and offers the bonus of potential major contributions to energy efficiency.

An added incentive to develop advanced ceramics, in fact the basis for their current market share leadership, is provided by Japan's burgeoning electronics industry. In both structural and functional applications, the electronics industry is currently by far the largest consumer of advanced ceramics, Table 12.2. Japanese firms are rapidly developing new products, miniaturizing existing components, and advancing product quality. The production of these high value electronic components not only provides current revenue for advanced ceramics, but more importantly, provides valuable learning curve and production scale experience which prepares current industry participants for the future, high volume, structural market.

The Japanese government and industry are intent upon developing the full spectrum of technology necessary to extend electronics

applications and to commercialize mechanical applications of advanced ceramics. If successful, this initiative would further enhance the competitive position of Japan's electronics industry and also secure technological leadership in the next generation of energy efficient oil and gas fueled power plants in automotive, industrial, and utility applications. Leadership in efficient energy conversion systems based upon fine ceramic technology would provide Japanese industry with a subsequent production cost advantage, minimize Japanese dependence on foreign imports of petroleum products and strategic materials such as cobalt and chromium, and secure extensive foreign markets for Japanese products such as automobiles, internal combustion engines, turbines, etc. Clearly, advanced ceramics offer Japan an opportunity to minimize its critical dependence on raw materials and foreign petroleum, and maintain or expand its economic growth and world market share upon which the health of the Japanese economy is based.

The Ceramics Substitution Dilemma

The consensus is that advanced ceramics are good candidates to replace a wide variety of strategic materials. Table 12.5 summarizes the range of market penetrations for selected applications as estimated by industry representatives.[12] The critical issue is "Which country will lead in high tech ceramic development -- the United States or Japan?" If Japan dominates in this materials sector, we may be faced with the dilemma of simply replacing one strategic dependence on platinum, chromium, cobalt,

Table 12.5. Structural Ceramic Market Penetration.[12]

Application	Market Penetration (%) by 2000	Market Penetration (%) by 2025
Transportation		
Diesel engines[a]	5-20	up to 50
Turbocharger parts	10-75	up to 80
Missile engine parts	5-50	up to 50
Cutting tools	5-10	10-25
Wear parts	5-30	15-40
Stationary turbine/diesel		
Small power generator	5-30	10-60
Large power generator	0-5	10-20
Heat recovery systems	50-70	75-95

[a]Combustion parts only; wear parts would be a higher penetration but less affected by the proposed program.

and manganese for another strategic dependence on Japanese advanced ceramics.

An Argonne National Laboratory study considered the potential impact of a U.S. or Japanese dominant scenario in advanced ceramics technology.[12] The major economic effects were:

- Gross National Product. In a U.S. Dominant scenario, the GNP was expected to be $28 billion (1981 $) higher in the peak year than in a Base Case forecast, or 0.6% higher than what could have been expected without the commercialization of ceramics. Conversely, in the Foreign Dominance scenario, GNP was projected to decline by $11 billion or 0.3% compared to the Base Case. In cumulative terms, real GNP was higher by $280 billion over the period 1985-2005 in the U.S. Dominant Case. In the Foreign Dominance Case, cumulative real GNP was projected to decline by $110 billion for the same period.

- Employment. Peak year employment was forecast to increase by 250,000 jobs in the U.S. Dominant Case, reducing the projected unemployment rate from 6.5% to 6.3%. In the Foreign Dominance Case, the importing of half a million foreign cars with ceramic engine systems resulted in a loss of over 100,000 jobs in the worst year.

- Balance of Trade. The use of structural ceramics in heat engines affects the balance of trade in two major areas -- imports of petroleum and imports of autos. In the U.S. Dominant Case, fuel savings continue as sales of new cars and trucks equipped with ceramic engines yearly increase the total size of the fleet that has the more efficient engines. Domestic production of these vehicles reduces the number of imported cars, which reaches a low point in the year 2000. Total import savings approach $28 billion (1981 $) in 2005. In the Foreign Dominance Case, the value of the imported cars exceed the value of the fuel savings so that there is a negative effect on the balance of trade, reaching $5.5 billion in 2005.

- Fuel Savings. Fuel savings are achieved under both scenarios, although the savings are greater for the U.S. Dominant Case. The greater energy savings are due to two assumptions: (1) broader market penetration (into stationary and heavy-duty engines for the U.S. case) and (2) a legislative limitation on the percent of imported cars (30% of new car sales) under the Foreign Dominance Case. Annuel fuel savings reach 1.1 quad by 2005 in the U.S. Dominant Case and 0.3 quad by 1995 (the peak year) in the Foreign Dominance Case.

These ranges of effects on the U.S. economy are principally the result of structural ceramic applications in vehicular engine systems and, to a small degree, of ceramic use in stationary power generation systems. It is recognized that a successful research program in basic structural ceramics technology will, in addition, have a substantial influence on other market areas for advanced ceramics including aerospace, weapons systems, electronic, optical, and refractory applications. Because these additional markets are likely to be quite significant spin-off applications from a structural ceramic research program for heat engines applications may be as important to the economy as the direct benefits from heat engine applications.

In short, advanced ceramics have the potential to not only replace strategic materials, but also to qualify as strategic and critical materials themselves.

References

1. Langer, M., Walzer, P., and Siebels, "Ceramic Component Development for Automotive Power Plants," Research Division of Volkswagenwerk AG, Postfach, 3180 Wolfsburg.1. West Germany.

2. Domenicali, D., "In Search of Better Ceramic Materials Processing," Electronic Business, May 1981, pp. 70-72.

3. Haggerty, J.S., "Sinterable Powder from Laser Driven Reaction," Energy Laboratory and Materials Processing Center, MIT, Report No. MIT-EL-82-002, Sept. 1981.

4. Haggerty, J.S., "Growth of Precisely Controlled Powders from Laser Heated Gases," Proceedings of the International Conference on Ultrastructure Processing of Ceramics, Glasses, and Composites, University of Florida, February 13-17, 1983, Gainesville, FL.

5. Barringer, E., Jubb, N., Fegley, B., Pober, R.L., and Bowen, H.K., "Processing Monosized Powders," Proceedings of Conference on Ultrastructure Processing, Hench and Ulrich, Eds., John Wiley (1983).

6. "High-Performance Fine Ceramics in Japan," Science and Technology in Japan, Under the Supervision of the Science and Technology Agency, Vol. 2, No. 8, October/December 1983, Quarterly, Tokyo, Japan.

7. "New Ceramics Market in Japan," Report, Yano Research Institute, Ltd., August 1982, distributed by Information Researchers, Inc., Suite 401, No. 59-4, Yoyogi 4-chome, Shibuya-ku, Tokyo 151, Japan.

8. Kenney, G.B. and H.K. Bowen, "High Tech Ceramics in Japan: Current and Future Markets," American Ceramic Society Bulletin, Vol. 62, No. 5, May 1983, pp. 590-596.

9. Mueller, J., "An Overview of Potential for the Substitution of Ceramic Materials for Vulnerable Materials and the Implications of National Materials Policy," Draft report, presented at Substituting Non-Metallic Materials for Vulnerable Materials, National Science Foundation, Washington, D.C., June 27-28, 1983.

10. Mueller, J., "Handicapping the World's Derby for Advanced Ceramics," American Ceramic Society Bulletin, Vol. 61, No. 5, 1982, pp. 588-590.

11. McLean, A.F. and E.A. Fisher, "Brittle Materials Design, High Temperature Gas Turbines, Final Report, AMMRC TR-81-14, Ford Motor Company, March 1981.

12. Johnson, L.R., Teotia, A.P.S., and L.G. Hill, "A Structural Ceramic Research Program: A Preliminary Economic Analysis," Center for Transportation Research, Energy and Environmental Systems Division, Argonne National Laboratory, Report no. ANL/CNSV-38, March 1983.

13. Lenoe, E.M., "Overview of DOD Ceramic Heat Engine Technology Projects," Proceedings of DOE/EMACC Meeting, Conf. 820911, Dept. of Energy, April 1983.

Appendix I. Material Supply

The use of ceramics in high technology applications depends strongly on the supply of materials. Although the basic ceramic raw materials occur abundantly in nature, they must be refined or processed before use in a manufacturing process. The entire group of silicon (Si)-based ceramics (other than silica, SiO_2) does not occur naturally: silicon carbide (SiC), silicon nitride (Si_3N_4), and sialon compositions all must be fabricated from gases and other ingrediants. Even minerals which occur naturally like Gibbsite, from which alumina (Al_2O_3) is derived, and zircon sands, from which zirconia (ZrO_2) is derived, must be processed before use to control purity, particle size and distribution, and general homogeneity of the powder. Table AP.1 lists a number of ceramic raw materials and their mineral source.

The structure of the ceramics industry is such that powder producers are usually vertically integrated. Raw materials are generally processed into powders and fabricated into component parts within a single company. This is particularly true of Si-based ceramics and some of the "new" zirconias. There are relatively few producers which supply ceramic raw materials and even fewer that supply new high tech ceramic powders.

Silicon-Based Materials

Silicon carbide and Si_3N_4 are the dominant silicon-based high tech ceramic materials. The traditional use of SiC has generally

Table AP.1. Ceramic Mineral Source.

Mineral Source	Ceramic Raw Material
Bauxite	Alumina Al_2O_3
Quartz, Silica rocksand sands Diatomaceous earth	Silica SiO_2 + Carbon SiC + Nitrogen Si_3N_4
Periclase, Magnesite Sea Water Brine	Magnesia MgO
Zircite, Baddeleyite Zircon sands	Zirconia ZrO_2

been broken down into the following categories: refractories, 10%; abrasives, 31%; and metallurgical applications, 59% (Table AP.2). In recent years, however, advanced ceramics applications have accounted for roughly 5% of the SiC consumed. Although detailed data for Si_3N_4 is not readily available, most of its applications are highly technical, requiring either high temperature strength, corrosion and erosion resistance, and/or good thermal shock resistance. The potential uses of both SiC and Si_3N_4, as well as the sialons, are many and varied. However, before new materials' markets can be entered, efficient processing techniques need to be developed to provide reproducible powder and reliable component parts.

Several methods have been developed to produce Si-based materials. Standard production processes for both SiC and Si_3N_4 are discussed in this section. An outline of the overall silicon-based ceramic production processes is provided in Figure AP.1.

Silicon Carbide

The reaction of silica sand with carbon produces SiC and carbon monoxide:

$$SiO_2 + 3C \rightarrow SiC + 2CO.$$

The carbon source is generally coke. Salt and sawdust are added to the reaction to create chlorides to purify the system and to aid in gas circulation, respectively. Low levels of alumina (Al_2O_3 - less than 0.25%) and iron oxide (Fe_2O_3 - less than 0.1%) must be maintained to control the undesirable formation of graphite and silicon metal.

Table AP.2. SiC Consumption by End Use, 1981.

Refractories	10%
Abrasives	31%
Metallurgical Applications	59%

The Acheson process for manufacturing SiC powder, the first commercial process, is carried out in a refractory furnace trough. A standard furnace is 24 meters long, 3 meters high, and 3 meters wide with a capacity of 25 tons. Carbon electrodes set at the ends of a refractory brick lining are connected by a graphite core which runs the length of tne furnace. This graphite core serves as both the carbon and heat source for the process. Electrical resistance heating of the graphite core brings the system to 2600°C. The furnace is then held at this temperature for 18 hours and then is allowed to cool slowly over a period of several days. An internal cylindrical layer of high grade SiC forms within two layers of an impure material with less than 70% SiC on the graphite core. These impure layers must be ground away to expose the high grade, crude SiC layer. Therefore, a series of grinding operations are required to recover and convert the usable layer into useful powder.

The Acheson process requires careful monitoring to insure the formation of usable SiC. Silicon carbide will dissociate if the temperature is too high: the silicon volatizes and the carbon reverts to graphite. Theoretically, the energy requirement is 5.75 Kwh/Kg crude SiC, but actual requirements are closer to 12Kwh/Kg. Work is underway to reduce the energy requirement, but this will require drastic process changes. Additional energy, approximately 1.5 Kwh, is required to produce a usable grade of grain SiC. Approximately 8-14 tons of high grade grain SiC can be produced from 75 tonnes of raw materials with an energy input of 13.5 Kwh / Kg.[2]

Current prices for SiC vary by grade and are available only for the traditional material used in abrasives, refractories, and metallurgical applications (Table AP.3). New production techniques for the manufacture of high grade, high purity powders for high tech applications are expensive. For example, a high-grade SiC substrate material for electrical uses has been developed in Japan and is in the price range of $200/Kg to 300/Kg.[3] Although several Japanese firms are marketing sinterable powder at $40/Kg, very little high grade SiC powder is available for commercial sale. Several domestic procedures of SiC industry feel if there was sufficient demand adequate supplies of high grade material could be made available.

Demand for advanced ceramics depends upon material properties, demonstrated engineering feasibility in applications, and cost. New powder production processes and improvements in the efficiency of traditional processes should reduce the cost of powders. Economics of scale can also be expected to reduce the cost of powders as production expands. Japanese producers estimate that they can reduce the total component cost to $28/Kg through better manufacturing techniques and to $18/Kg with improved, low-cost powders. New powder processing technology will provide better quality control and improved component performance and reliability.

Research has focused on producing sinterable grades of SiC to accommodate near net shape processing techniques. Earlier fabricating processes, constrained by the low sinterability of SiC, have been limited to the costly hot pressing technique which produces a component requiring diamond machining to meet final specifications. Sinterability can be enhanced with dopants,

Table AP.3. Prices of Silicon Carbide: 1970 to 1980.*
(Kg, 8-220 mesh, cif)

Date	Abrasive grade	Black 99% SiC	Green 99.5% SiC
1970 - Nov. 1972	$0.41	...	...
Dec. 1972	0.51	...	...
Mar. 1973	0.53	...	...
Feb. 1974	0.56	...	...
Oct. 1974	0.85	...	...
Mar. 1975	1.05	...	...
May 1975	...	0.92	1.17
May 1976	...	0.90	1.14
May 1978	...	1.20	1.52
Nov. 1979	...	1.35	...
Nov. 1980	...	1.69	2.07

Adapted from Reference 2.

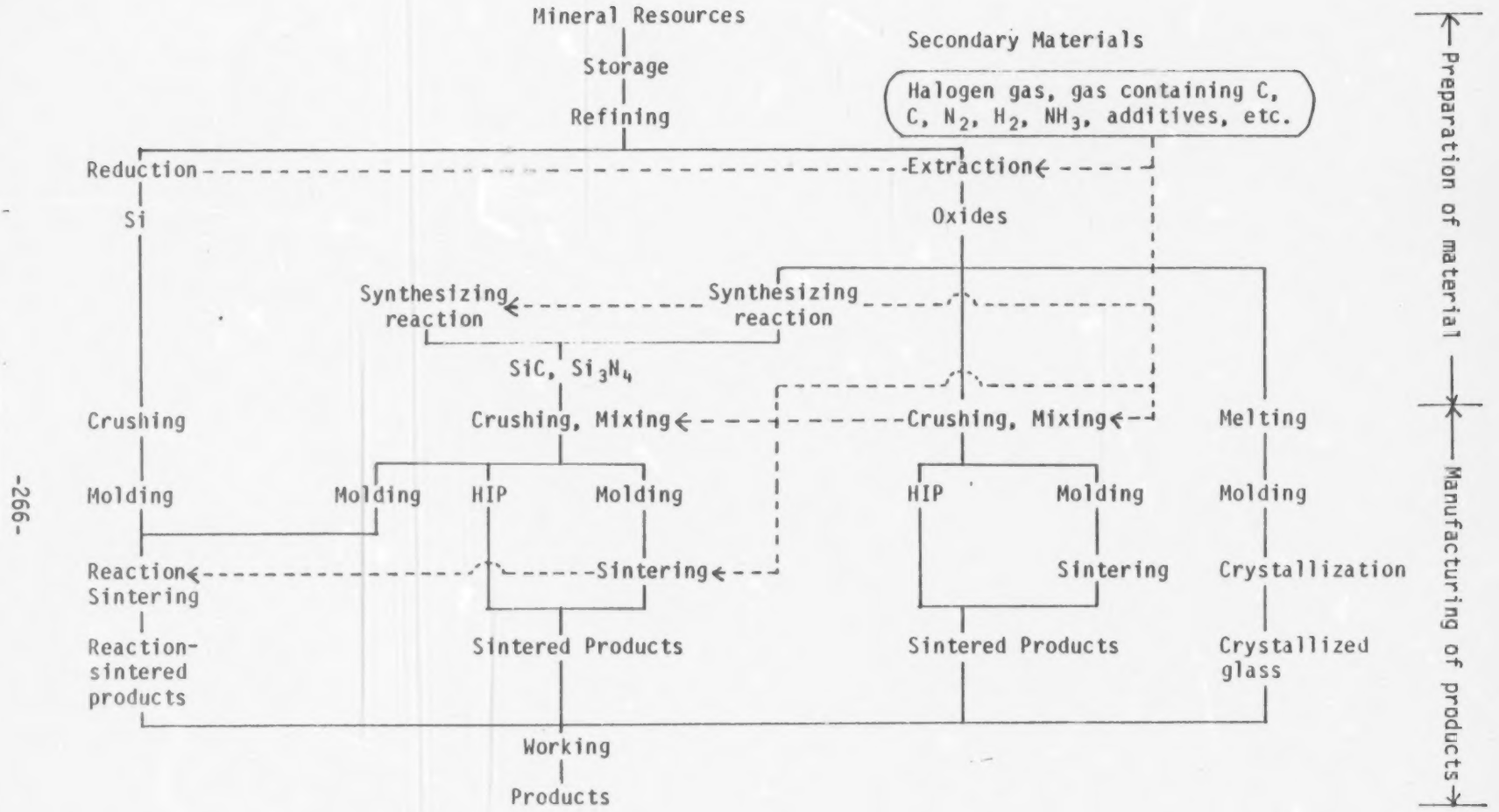


Figure AP.1. Outline of production processes of fine ceramics.[3]

additives which can control particle rearrangement and diffusivities. These dopants allow sintering processes to occur at lower temperatures and/or at faster rates. Dopants are also used to control grain growth or achieve higher final densities. The use of dopants, while providing many beneficial results, can also influence materials' properties. Segregation of impurities to the grain boundary can weaken a final part, and final properties (conductivity, strength, etc.) may vary significantly from the "pure" material.

One new powder processing technique is the laser induced, gas phase synthesis of ceramic powders. This process reacts silane (SiH_4), a by-product of petroleum refining, with ethylene (C_2H_4) to produce SiC powder:

$$SiH_4 + 1/2\ C_2H_4 \rightarrow SiC + 3H_2.$$

Cost estimates for this process are included at the end of this section. These estimates are based on cheap, readily available SiH_4, \$2/Kg to \$20/Kg. Current prices for SiH_4 range as high as \$100/Kg to \$200/Kg. Increased demand, however, should increase the supply of SiH_4 and reduce its cost. Low grade SiH_4, requiring less refining and, therefore, lower in cost, could be used in this process. Laser synthesis provides a means of producing high grade, high purity, monosized, homogeneous powders at a potentially low cost (less than \$20/Kg)[4].

Silicon Carbide Fibers

A growing area of ceramics research focuses on ceramic/ceramic composites. A number of fibers, such as Al_2O_3, boron nitride (BN),

SiC, and glass, have been used to reinforce ceramic materials. The major candidate for ceramic fiber reinforcement (other than fiber glass) is SiC fiber. When imbedded in a ceramic matrix, these fibers can improve fracture toughness two to five times while maintaining high strength[5]. As yet, ceramic/ceramic fiber composite processes are only in the experimental stage.

Silicon carbide fiber production is similar to graphite fiber production, which involves the basic technique of polymer pyrolysis. Silicon chemicals are wet-chemistry processed to manufacture polycarbosilane and polyborosiloxane-based silicon polymers. The silicon polymers are then distilled, and melt spun. After spinning the polymers are cured by heating in air. The fiber is then pyrolized in vacuum or an inert atmosphere to produce a low density SiC fiber. Silicon carbide fibers are also produced by a chemical vapor deposition process which deposits silicon metal on graphite fibers. The resulting fibers are much thicker than those produced using polymer pyrolysis techniques. Silicon carbide whiskers have also been produced from rice hulls. Whiskers have strengths which are close to theoretical values, but this is currently only a laboratory procedure.[6]

At the present time, SiC fibers are commercially available only from Japan through a domestic distributer at a cost of approximately $215/lb. All are being sold for research and development purposes. Some projections indicate that a long-term fiber price of approximately $100/lb is not unreasonable. Work to manufacture SiC fibers by polymer pyrolysis in this country is underway, but as yet there is no commercial product.[7]

Ceramic fiber composites have the potential to create a class of materials with a combination of high modulus, high strength, and reasonable fracture toughness. Commercial application will require the production of a wide range of fiber grades. While some experimental methods show promise, composite manufacturing processes on the whole require further development. The potential for structural ceramic/ceramic composite applications, while not near-term, could become viable in the next 5-15 years.

Silicon Nitride

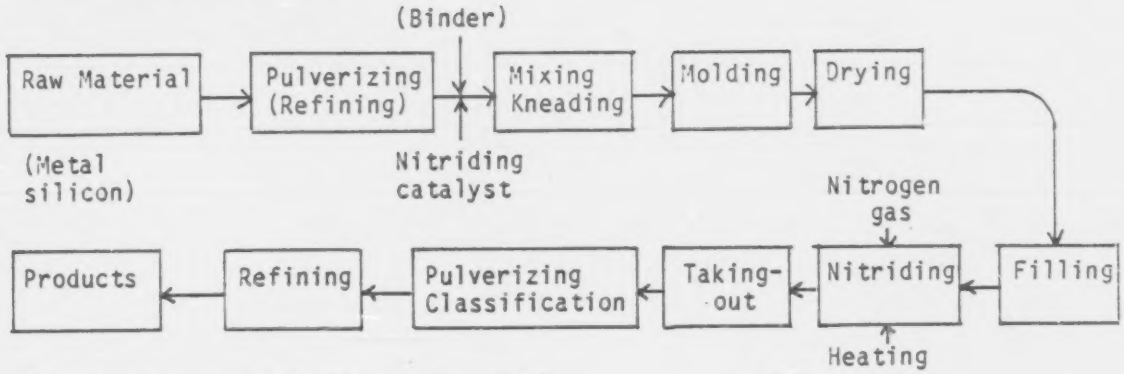
Silicon nitride (Si_3N_4) is most commonly produced by the direct nitriding method:

$$3\ Si + 2\ N_2 \rightarrow Si_3N_4.$$

The reaction occurs at 1450°C and must be carefully controlled to generate high quality material. Figure AP.2 illustrates other Si_3N_4 production techniques. The silica reduction method is currently in use, while the vapor phase synthesizing method is in the experimental stage.

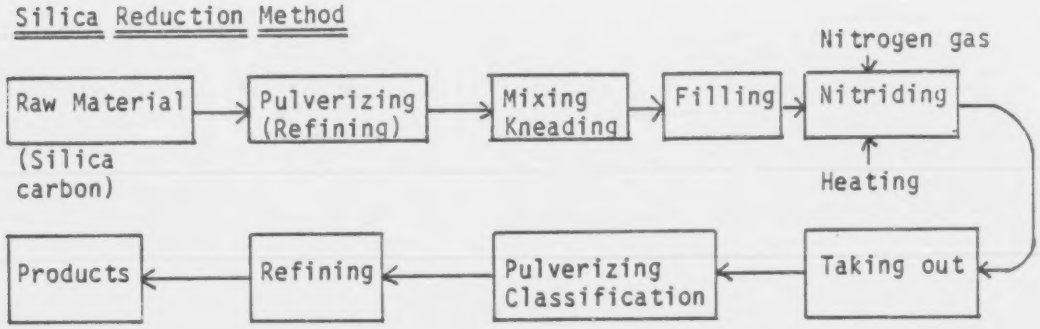
Silicon nitride components are available in two forms: reaction-bonded and hot pressed. The reaction-bonded form of Si_3N_4 has the major advantage of less than 1% shrinkage during firing. This allows for a variety of near-net shape processing techniques and eliminates expensive machining operations. The basic reaction-bonding process requires an initial porous shape produced from either isostatically pressing, slip casting, injection molding, or extruding starting powders. The shape is then dried and nitrided.

Direct Nitriding Method



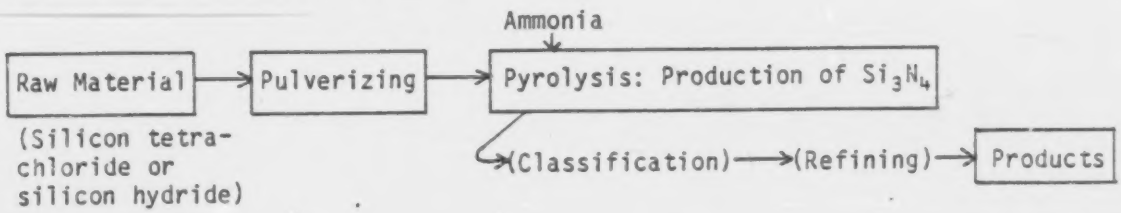
[Chemical equation] $3Si + 2N_2 \rightarrow Si_3N_4$

Silica Reduction Method



[Chemical equation] $3SiO_2 + 6C + 2N_2 \rightarrow Si_3N_4 + 6CO$

Vapor Phase Synthesizing Method



[Chemical equations] $3SiH_4 + 4NH_3 \rightarrow SiN_4 + 12H_2$
$3SiCl_4 + 16NH_3 \rightarrow Si_3N_4 + 12\ NH_4Cl$
$3SiCl_4 + 4NH_3 \rightarrow Si_3N_4 + 12HCl$

Figure AP.2. Production of silicon nitride.[3]

Nitriding techniques, inducing an initial consolidation of the material, allow it to be green-machined at intermediate stages before being sintered to a high final density. Reaction-bonded components are porous; actual final densities are lower than those of sintered Si_3N_4.

Hot pressed Si_3N_4 is manufactured from Si_3N_4 powder doped with materials such as magnesia (MgO) or yttria (Y_2O_3) which aid in densification. The powder is placed in a graphite die, induction heated to 1750°C, and pressed at pressures up to 23MN/m^2. This process yields blocks of high density, non-porous material. As in other hot pressing operations, the product requires expensive diamond machining. Therefore, although this method produces a high quality product with high strength, low porosity, and reasonable toughness, its total cost is rather high. New techniques for processing Si_3N_4 include experiments with sinterable grades of powder, laser synthesis of powders, and new machining methods.

The current demand for Si_3N_4 products is small. The major domestic product is reaction-bonded Si_3N_4 welding nozzles. The Japanese, however, are currently marketing Si_3N_4 glow plugs, swirl chambers, and turbochargers. Glow plugs are produced for diesels in volumes of 30,000/mo. and are priced at approximately $10/plug. Swirl chambers, currently manufactured at approximately 20,000/mo., could be priced as high as $40/lb; this venture, however, is presently losing money.[12] At the present time, Si_3N_4 powder is unavailable from domestic commercial sources. A limited number of Japanese producers provide Si_3N_4 powders for sale at approximately

$40/Kg for prototype parts fabrication and other experimental purposes. In spite of the many potential applications for this material, the current annual market is less than $0.5 million. The majority of Si_3N_4 parts manufactured are extremely expensive and are not competitive with other existing materials (with the exception of cutting tools and welding nozzles). However, research is currently underway to reduce the cost of Si_3N_4 parts and to find new manufacturing techniques. Developing markets for these materials is an iterative process. Feasible applications must be assessed to determine where the market is and what it can bear for the enhanced properties and performance. Future reductions in cost will occur as process research continues and economies of scale accumulate.

Sialon

Sialons are new materials based on the elements of silicon, aluminum, oxygen, and nitrogen (SiAlON). Two of the benefits of this class of material are ease of fabrication, relative to Si_3N_4, and oxidation resistance. Several methods exist for producing sialon powders. Varieties of the sialon family are produced from different combinations of silicon nitride and alumina, aluminum nitride and silicon, and others. Sialon components can be fabricated by a number of techniques, including pressing operations, slip casting, injection molding, and hot pressing. These components can be sintered in an inert atmosphere to high densities or hot pressed. Sialon materials are still in the developmental stage (except for cutting tool applications), but the market has a large

potential for growth and expansion. The potential markets for sialon included expand use as a cutting tool material, frictionless pistons in diesel engines, seals, and other applications where SiC and Si_3N_4 cab be used.

Alumina

Although alumina (Al_2O_3) is a naturally occuring mineral [Gibbsite, $Al)OH)_3$], a number of processing steps must be carried out before it can be used in high tech ceramic applications. The major use of alumina, 90% of that mined, is in the production of aluminum metal; the other 10% is used in a variety of traditional and high tech ceramic processes (Table AP.4).

Alumina (α - Al_2O_3) is produced by the Bayer process in which minerals such as bauxite are pulverized, melted with soda, seperated, and calcined (Figure AP.3). Another method of alumina production is alkoxide hydrolysis in which aluminum metal is synthesized to aluminum alkoxide, then to an aluminum hydroxide and calcined to produce Al_2O_3 and water. The alumina produced is available as alpha aluminum trihydrate [α - $Al(OH)_3$], calcined alumina, and a variety of lower grades.

Demand for alumina is a function of general economic conditions. Prices for Bayer alumina are generally cost-driven and range from $0.22/kg - $1.36/kg in 1982. Bayer alumina is used in most of the traditional applications, and alumina production capacity based on current demands, is more than adequate through 1990. There is a demand for high purity alumina for a number of high tech applications such as electronic substrates, catalyst

Table AP.4. Domestic Alumina Consumption in the Ceramic Industry by End-Use, 1981.[9]

End-Use	Percent Consumption
Refractories	30
Abrasives	25
Whitewares and Spark Plugs	25
Ceramics (80 + % Al_2O_3)	10
Glass and Enamels	5
Other	5

$Al(OH)_3$ Calcining Method (Bayer process)

Caustic soda — Water

Raw material (Bauxite) — Pulverization — Melting — Separation of aqueous solution of residue — Deposition of Alumina

Products — Burning — Washing

[Chemical equation]

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$$
$$NaAl_2O_2 + 2H_2O \rightarrow NaOH + Al(OH)_3$$
$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

Alkoxide Hydrolysis Method

Water

Raw Material (Metal Aluminum) — Synthesis of alkoxide — Hydrolysis (Aluminum hydroxide)

Burning — (Classification) — (Refining) — Products

[Chemical equations]

$$Al + 3ROH \rightarrow Al(OR)_3 + 3/2H_2 \quad \text{(Synthesis of alkoxide)}$$
$$Al(OR)_3 + 3H_2O \rightarrow Al(OH)_3 + 3ROH \quad \text{(Hydrolysis)}$$
$$2Al)OH)_3 \rightarrow Al_2O_3 + 3H_2O \quad \text{(Burning)}$$

Figure AP.3. Alumina production techniques.[3]

supports, seals, nozzles, cutting tools, and coatings. Alumina produced for many of these uses requires further refinement and purification beyond that available with the Bayer process. Prices for high purity alumina can be as much as ten times that for Bayer alumina. The supply of alumina appears adequate; however, some of the markets for alumina are being penetrated by alternate materials. Silicon carbide is now a good candidate to replace alumina in the area of substrates because of its higher thermal conductivity and electrical resistivity. It is also being used in some of the traditional applications of high grade alumina such as seals and nozzles. Silicon nitride is penetrating the cutting tool market which may reduce the use of both Al_2O_3-coated cutting tools and Al_2O_3 tool inserts. To date, Al_2O_3 has maintained a cost advantage over SiC and Si_3N_4 for these applications. However, as the quality and performance of Si-based ceramics improves and production costs decrease, Al_2O_3 can be expected to lose part of its current market share.

Zirconia

Zirconia (ZrO_2) powders are produced as natural by-products in copper/phosphate/magnetite and baddeleyite mining. They can also be produced from zircon ($ZrSiO_4$) sands or chemical hydrolysis.

Traditionally, zirconia has been used in refractories and abrasives (Table AP.5). Newer applications focus on electronic properties such as capacitance and the piezoelectricity of zirconate titanate bodies. These new applications include oxygen sensors in

Table AP.5. Domestic Zirconia Consumption by End-Use 1981.[9]

End-Use	Percent Consumption
abrasives	50
refractories	33
ceramic color industry	7
electronic	6
glass and synthetic gems	4

automobiles and industrial furnaces, components in continuous steel casting operations (crucibles, nozzles, and tubes), and protective coatings such as thermal barriers. Demand in these areas has remained fairly constant. Due to zirconia's transformation toughening abilities which impart higher fracture toughness, research interest in the development of new structural applications in engine applications has been high. Zirconia's toughening abilities are due to phase changes which are temperature and processing dependent.

In order for zirconia to be used in high temperature, structural applications, it must be stabilized or partially stabilized to prevent a monoclinic - tetragonal phase change which is accompanied by a greater than 4% change in volume. Stabilization involves the addition of calcia, magnesia, or yttria followed by some form of heat treatment. A flow diagram of zirconia production from sand to finished product is illustrated in Figure AP.4.

The properties of the stabilized zirconia vary substantially with the additive, type of heat treatment, and percent of stabilization (Table AP.6). Both calcia and magnesia are inexpensive; however, yttria, which is currently thought to provide greater temperature stability, fatigue resistance, and possibly higher fracture toughness, is more expensive. Current market prices for yttria-stabilized ZrO_2 are as high as $32/lb, while magnesia-stabilized material is $8/lb.

The supply of partially stabilized zirconia (PSZ) powders for commercial use is not abundant. Several Japanese firms, a few

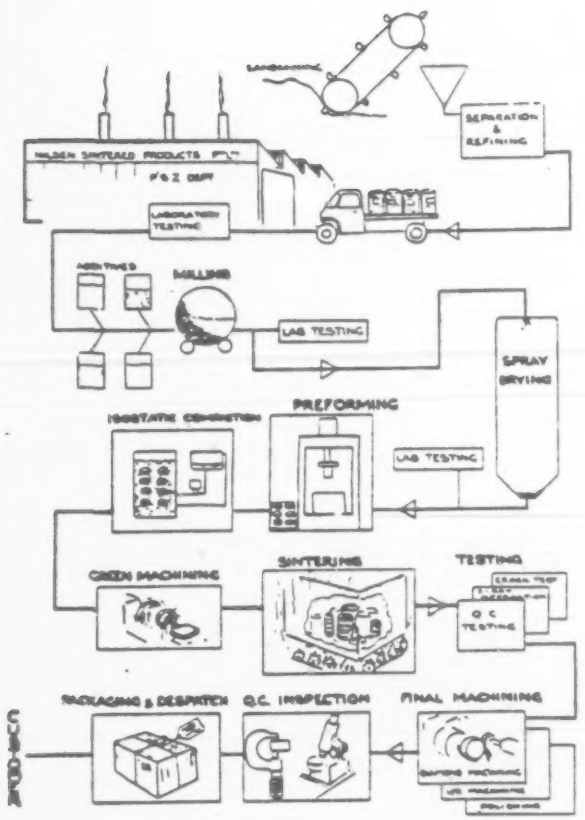


Figure AP.4. Schematic flow diagram showing PSZ powder processing route.[11]

Table AP.6. Mechanical Property Comparison
Polycrystalline PSZ.

Material	ρ (g/cm³)	H (GPa)	σ (MPa)	K_{IC} (MPa-m$^{1/2}$)	γ_f (J/m^2)	E (GPa)	γ	ΔT_c (°C)	Microstructure and XRD Phase Analysis
A. JAPAN (Y_2O_3)	5.75	11.7	900	4.7	50	201	0.32	375	0.1 - 0.5 μm 2-10μm duplex, cubic, tetrag. same monoclinic
B. AUSTRALIA (MgO)	5.75	9.4	700	>8-15	>160	200	0.24	425	10.40 m, 0.1-0.3 μm precipitates; cubic, tetrag., monoclinic
C. GERMANY (Y_2O_3)	5.77	11.6	650	>7 - 8 -15	>120 >500	209	0.31	325	similar to "B".
D. U.S.A. (Y_2O_3)	5.24	11.0	200	2.7 - 2.9	21.25	170	0.29	-	5-20 μm, no precipitates cubic ?
E. U.S.A. (M_2O)	5.08	10.3	300	6.0 - 6.1	111 - 115	162	0.27	350	1-10 μm, 0.1 μm precipitates monoclinic, cubic and tetragonal
F. U.S.A. (M_2O)	-	9.2 -11.5	430	4.7	60	192	0.30	225	55 μm, precipitates 0.1 - 0.3 μm

FROM: U.S. NAVAL RESEARCH LABORATORIES

American companies, one West German company, and one Australian company supply the United States market. The industry structure is vertically integrated and powder producers generally manufacture parts from stabilized powder rather than sell the powder directly.

Summary

Many other ceramic materials are used in a variety of traditional and high tech applications. The raw materials are generally abundant; fine powders, however, tend to be less readily available. There is also a significant variation in the quality of commercially available high grade powders. Differences exist in chemical composition, particle size, shape, and particle size distribution, all of which influence the final properties and performances of components. These differences, while not critical to the production of refractory bricks or abrasives, are extremely important in the production of fine structural ceramics. Initial powder characteristics influence the overall reliability and reproducibility of the fabricated component. Therefore, before the ceramics market realizes its full potential, a supply of high purity, homogeneous, uniform powders will be required.

While it is true that the raw materials are inexpensive, the refining and fabrication processes can be extremely expensive. After powder refinement, several value-added operations must be included in the manufacture of a part. Final finishing procedures, including diamond machining, can be extremely expensive (as high as 38% of the total cost for turbine blades). Rejection rates for

finished parts are also extremely high, ranging from 25%-75%. Future demand will depend upon the perceptions of ceramic reliability and reproducibility. Further development of ceramics powders, manufacturing techniques, and finishing and inspection techniques must be made. Traditional markets for ceramics fluctuate with general economic trends; however, the market for new advanced ceramics will depend upon supply/demand relationships and consumer perceptions of the materials themselves.

References

1. Stephan, P.M., Principal Research Scientist, Batelle Columbus Laboratories, Personal Communication (June, 1983).

2. "The Economics of Silicon Ceramics (Silicon Carbide, Silicon Nitride, and the Sialons)," Roskill Information Services, Ltd., London, England, November 1981.

3. "Fine Ceramics," Fine Ceramics Office, Japan, Nov. 1982.

4. Haggerty, J., "Laser Synthesized Ceramic Powders," Unpublished, 1982.

5. Rice, R.W., "Ceramic Composites - Processing Challenges," Ceramic Engineering and Science Proceedings, Vol. 2, No. 7-8 (1981): .

6. Williams, W., University of Illinois, Personal Communication, July, 1983.

7. Didrichson, P., Dow Corning, Personal Communication (July, 1983).

8. Burke, J.J., Gorum, A.E., Katz, R.N., "The Sialons - Properties and Fabrication," in Ceramics for High Performance Applications, Arrol, W.J. ed., (Chestnut Hill, MA:Brook Hill Publishing Co., 1974), p. 729.

9. "Annual Ceramic Mineral Resources Review," American Ceramic Society Bulletin, Vol. 62, No. 5 (1983).

10. Kamo, R., "High Technology Ceramics for Japanese Heat Engines," Report Draft, Division of Policy Analysis, Advanced Technologies and Resources Policy Group, National Science Foundation, April 1983.

11. Marmach, M., Serveul, D., Hannick, R.H.T., Murray, M.J., and Swain, M.V., "Toughened PSZ Ceramics - Their Role as Advanced Engine Components," Report, SAE No. 830318, Warrendale, PA, 1983: 65-71.

12. Bowen, H.K., "Technology Base for Japan's Ceramic Thrust," Unpublished Draft, M.I.T., August 1983.